POLYNUCLEAR AROMATIC HYDROCARBONS in AIR by GC-MS SIM 5528

Formulae: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 5528, Issue 1 **EVALUATION:** FULL **Issue 1:** November 2021

OSHA: Table 3
NIOSH REL: Table 3

PROPERTIES: Table 2

SYNONYMS: Table 1

SAMPLING

SAMPLER: Filter + Sorbent tube (glass fiber filter, OVS-7 tube: 13-mm; XAD-7, 200 mg/100 mg)

FLOW RATE: 1 L/min

VOLUME MIN: 1 L
VOLUME MAX: 480 L (see Method Evaluation)

SHIPMENT: Protect from light; standard

SAMPLE STABILITY: at least 30 days at < 4°C [1]

BLANKS: 10% (≥ 2) of samples

ACCURACY [1]

RANGE STUDIED: 0.25 to 75 µg/sample. Table 7

BIAS: Table 7

OVERALL PRECISION ($\hat{S}_{rT}$): Table 7

ACCURACY: Table 7

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY-MASS SPECTROMETRY SELECTED ION MONITORING GC-MS SIM

ANALYTE: Table 1

INJECTION VOLUME: 1 µL Splitless

CARRIER GAS: Helium @ 1.3 mL/min

COLUMN: Phenyl arylene polymer (0.5 µm) film fused silica capillary column (30 m × 0.32 mm ID)

MASS SPEC: Tables 5 and 6

CALIBRATION: At least six media-spiked standards to cover the range

ESTIMATED LOD: 0.08 to 0.2 µg/sample (Table 8)

PRECISION ($\bar{S}_r$): Table 9

APPLICABILITY: For analysis of PAHs in air. The working range for a 240-L air sample is 0.0011 to 2.0 mg/m^3.

INTERFERENCES: Because of the mass-selective capabilities of GC-MS, interferences are not anticipated to have any impact on the analysis. At higher humidity levels (80% and above), the method range is shortened as samples at concentrations of 10 µg/sample do not quantitatively recover.

OTHER METHODS: This method is similar to NIOSH 5515, with primary differences including a more efficient sampling device and the use of GC-MS SIM rather than GC-FID [2]. NIOSH 5506 (HPLC) uses the same sampling technique as NIOSH 5515 [3]

REAGENTS:

1. Desorbing solvent: Methylene chloride. High Purity grade or equivalent.
2. Dilution solution: Methylene chloride containing approximately 1 µg/mL of internal standard(s). Prepare by adding 100 µL of internal standard spiking solution to exactly 10 mL of methylene chloride. (Do not reduce volume to compensate for the 100 µL added.)
3. Internal standard spiking solution: naphthalene-D_8, acenaphthene-D_{10}, phenanthrene-D_{10}, chrysene-D_{12}, and perylene-D_{12} at about 100 µg/mL in methylene chloride.
4. 16 PAHs, 1000 µg each in 1 mL solvent: Naphthalene, Acenaphthylene, Acenaphthene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[ghi]perylene, Benzo[k]fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno[1,2,3-cd]pyrene, Phenanthrene, Pyrene
5. Helium, UHP (carrier gas for GC-MS)

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: OVS-7 sampling tube with glass fiber filter (glass tube, 11-mm i.d. × 13-mm o.d. × 50-mm long, with the outlet end drawn to a 6-mm o.d. × 15 to 25-mm-long tube. The enlarged part of the tube contains a 200-mg front section of 20/60 mesh XAD-7 sorbent held in place by an 11-mm o.d. glass fiber filter (GFF) and a polytetrafluoroethylene (PTFE) retaining ring. The front section is separated from the back section of 100-mg XAD-7 sorbent with a short plug of polyurethane foam (PUF). The back section is held in place by a long plug of PUF. The sampler is available commercially (See Figure 1).
2. Personal sampling pump, 0.5 to 2 L/min, with flexible connecting tubing
3. 4-mL Amber glass vials with caps
4. 2-mL Amber GC vials with caps
5. Gas chromatograph-mass spectrometer capable of selected ion monitoring, column, autosampler, and data integrator (page 5528-1)
6. Microliter syringes
7. Ultrasonic water bath
8. Foil for shipping

SPECIAL PRECAUTIONS: Wear gloves, lab coat, and safety glasses while handling all chemicals. All work should be performed in a fume hood. Treat benzene, methylene chloride, and all polynuclear aromatic hydrocarbons as carcinogens. Neat compounds should be weighed in a high efficiency fume hood or glove box. Spent samples and unused standards are toxic waste. Regularly check countertops and equipment with "black light" for fluorescence as an indicator of contamination by PAH.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Connect the sampler to personal sampling pump with flexible tubing. The sampler should be placed vertically with the large end down, in the worker's breathing zone, in such a manner that it does not impede worker performance. Follow manufacturer's instructions on use of OVS tube and holder.
3. Sample at an accurately known rate around 1 liter per minute for a total sample size of 1 to 480 liters (maximum = 480 liters).
4. Upon completion of sampling, immediately cap both ends of the sampler and protect from light by wrapping in foil. Pack securely for shipment.

SAMPLE PREPARATION:

5. Transfer the glass fiber filter and the front section to a 4-mL amber glass vial (C_f). Transfer the back section and foam plug which separates the front resin from the back resin (C_h) to a second 4-mL amber glass vial.
6. Add 2 mL of methylene chloride to each vial. Cap the vial and shake well, then place in an ultrasonic bath for at least thirty minutes.
7. Transfer an accurately measured aliquot of the desorbing solvent to a GC vial (e.g., 1.0 mL).
8. Spike with the internal standard spiking solution to achieve an internal standard concentration of approximately 1 µg/mL (for example, spike 10 µL of internal standard solution into a 1.0 mL aliquot of desorption solvent).

CALIBRATION AND QUALITY CONTROL:

9. Calibrate with at least six working standards covering the expected concentration range of the samples.
   a. Prepare each working standard by spiking a known amount of stock solution onto the glass fiber filter and front XAD-7 resin from a blank OVS-7 sampler contained within a 4-mL amber glass vial.
   b. Add 2 mL of methylene chloride to each vial and desorb in the same manner as the field samples (steps 5-8 above).
   c. Prepare at least two method blanks by adding 2 mL of methylene chloride to the glass fiber filter and front XAD-7 resin from a blank OVS-7 sampler contained within a 4-mL amber glass vial and desorbing in the same manner as the field samples.
   d. Analyze calibration standards and method blanks with field samples and laboratory control samples (steps 11-12).
   e. Prepare calibration graphs by plotting, for each working standard, the analyte relative response (peak area of analyte divided by the peak area of the internal standard in the same chromatogram) on the y-axis vs. concentration of analyte on the x-axis. A linear or quadratic model may be utilized in processing the analytical data. Quadratic models usually work best on GC-MS data. To confirm acceptability of the calibration curve, when each standard is inserted into the calibration equation, the value should be within ±20% of the expected value.
   f. Prepare laboratory Quality Control samples in duplicate with each sample set.
   g. Independently prepared quality control PAH solutions in dilution solution must be prepared at concentrations within the analytical range.
   h. Remove the cap from the large end of a sampler tube. Apply solution to face of glass fiber filter (GFF).
      NOTE: Spiking volume should not exceed 25 µL otherwise there might be wicking of the spiking solution to the edges of the GFF and then behind the PTFE retainer ring. One way to avoid this is to pull the retainer ring away from the GFF by a few millimeters prior to spiking the GFF.
   i. Re-cap the samplers and allow to stand for a minimum of one hour. Transfer to a 4-mL amber glass vial and desorb in same manner as the field samples (steps 5-8).
   j. Analyze these along with the field samples, blanks, and calibration standards (steps 11–12). QC values should normally be within ±20% of the spiked values. If not, the batch is considered out of control, the batch data discarded, and corrective actions taken before more samples are analyzed.

MEASUREMENT:

10. Set gas chromatograph and mass spectrometer according to manufacturer's recommendations and to conditions given on page 5528-1 and in Table 5.
11. Inject sample aliquot with autosampler or manually (using solvent flush technique is not necessary if internal standards are used). See Table 4 for retention times of selected analytes.

NOTE: If peak area is greater than the range of the working standards, dilute an aliquot of the sample with desorbing solvent and reanalyze. Apply appropriate dilution factor in calculations.

12. Measure peak areas of analyte and internal standard and compute analyte relative peak area by dividing the peak area of the analyte by that of the internal standard in the same chromatogram.

CALCULATIONS:

13. Determine the concentrations of the target analytes in µg/sample of respective analyte found in the sample front section (C_f) and back section (C_b), and in the media blank front (B_f) and back (B_b) sections from the calibration graph.

    NOTE: If C_b is greater than $C_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(C_f + C_b) - (B_f + B_b)}{V} \text{ mg/m}^3 \text{ x dilution factor (if any)}$$

EVALUATION OF METHOD [1]:

Precision and accuracy were evaluated over six spiked concentration levels from 0.25 to 75 µg/sample. This range represented 1x the estimated analytical LOQ to 300× the estimated LOQ. Seven replicates were analyzed at each level. Precision and accuracy are given in Table 7. Data were not included where desorption was <75% or >125%. This meant the lower 4 levels of Acenaphthylene (0.25 µg-7.5 µg) and the lowest level of Benzo[a]pyrene (0.25 µg) were omitted. For definitions and mathematical formulae used for precision, accuracy, and bias, refer to the backup data report [1].

The average recoveries at the various concentration levels are shown in Table 8; the data not used for precision and accuracy are in bold type.

Sample storage was evaluated up to 30 days at two different temperatures. OVS-7 samplers were spiked with 75 µg/sample for each PAH. Spiked samplers were stored at ambient temperature and at 4° C for 7, 10, 14, 21, and 30 days and then analyzed. Recoveries for all analytes up to 30-day storage at both temperatures were above 80%.

OVS-7 sampler capacity or breakthrough was determined for up to 24 hours at 1-liter air per minute. No breakthrough was detected for any analyte up to the maximum time tested. All analytes appeared to be stable in storage up to 30 days on the OVS-7 sampler, but acenaphthylene exhibited breakdown during sampling over long time periods. Recoveries were 93% in 8 hours but dropped rapidly to about 80% in 16 hours and to 74% in 24 hours. Therefore, it is recommended to sample for no more than 8 hours. Otherwise, acenaphthylene will be biased low due to degradation during sampling. Acenaphthenone was detected in the samples showing reduced recoveries for acenaphthylene.

The LOD and LOQ were determined by analyzing a series of standards with the data fitted to a quadratic curve [1]. The LOD and LOQ were estimated according to the Burkart Method [4]. Estimated LODs are given in Table 8. The limits of detection for this method are on average (except for anthracene) twice as low as for NIOSH 5506. The LOD for anthracene is comparable to NIOSH 5506 [3].

A humidity challenge was done at 10, 48, 96, and 192 µg per sample (n = 6) with a mixture of 16 PAHs at 80% relative humidity [1]. Humid air was pulled through the loaded samples at 1 L/min for 8 hours. The samplers sat overnight before analysis. A Tukey [1] multiple comparison test indicated that the 10-µg level

was statistically different from the other three levels; 70.5 to 78.5, 90.0 to 104.0, 78.0 to 86.0, and 80.9 to 87.8% average recovery for the 16 PAHs at 10, 48, 96 and 192 µg per sample respectively.

A user check tested the method over the range of 0.5, 2.0, 5.0, and 20.0 µg per sample (n = 6) [1]. 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). A humidity challenge was also done, with 10, 48, 96 and 192 µg samples at 80% relative humidity. As in the humidity challenge done during method development, the 10-µg samples were lower than 80% recovery.

REFERENCES:

[1] NIOSH [2005]. Back-up data report: Polynuclear aromatic hydrocarbons in air by GC-MS SIM. https://www.cdc.gov/niosh/nmam/datadoc.html

[2] NIOSH [2003]. Method 5515: Polynuclear aromatic hydrocarbons by GC. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods. 4th edition. Cincinnati, OH: U.S. 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 [2003]. Method 5506: Polynuclear aromatic hydrocarbons by HPLC. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods. 4th edition. Cincinnati, OH: U.S. 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] Burkart JA [1986]. General procedures for limit of detection calculations in the industrial hygiene chemistry laboratory. App Ind Hyg *1*(3):153-155.

[5] Rumble J [2019]. Handbook of physical properties of organic chemicals. Boca Raton, Florida: CRC/Lewis Publishers. https://hbcponline.com

[6] NIOSH [1987]. Registry of toxic effects of chemical substances. U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-114.

[7] O'Neil M, ed. [2013]. Merck Index, 15th ed. Rahway, New Jersey: Merck and Co., Inc. https://www.rsc.org/merck-index

[8] ACGIH [2020]. TLVs and BEIs based on the documentation of the Threshold Limit Values for chemical substances and physical agents and Biological Exposure Indices. Cincinnati, Ohio: American Conference of Governmental Industrial Hygienists. https://www.acgih.org

[9] NIOSH [1992]. NIOSH recommendations for occupational safety and health. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication. No. 92-100.

[10] Kim S, Chen J, Cheng T, Gindulyte A, He J, He S, Li Q, Shoemaker BA, Thiessen PA, Yu B, Zaslavsky L, Zhang J, Bolton EE [2019]. PubChem 2019 update: improved access to chemical data. Nucleic Acids Res. 8(47):D1102-D1109. https://pubchem.ncbi.nlm.nih.gov/

METHOD WRITTEN BY:

Dawn Farwick, NIOSH. Method developed by DataChem Laboratories, Inc., Salt Lake City, Utah under NIOSH Contract CDC-200-2001-0800.

Table 1. CAS Numbers, RTECS Numbers, and Synonyms

Compound (alphabetically)	CAS Number	RTECS Number(1)	Other Names(2)
Acenaphthene	83-32-9	AB1000000	1,2-dihydroacenaphthylene; 1,8-ethylenenapthylene
Acenaphthylene	208-96-8	AB1254000	Acenaphthalene; cyclopenta[de]naphthalene
Anthracene	120-12-7	CA9350000	
Benz[a]anthracene	56-55-3	CV9275000	1,2-benzanthracene; 2,3-benzphenanthrene; tetraphene
Benzo[b]fluoranthene	205-99-2	CU1400000	3,4-benzfluoranthene; 2,3-benzofluoranthene; benz[e]acephenanthrylene
Benzo[k]fluoranthene	207-08-9	DF6350000	benzofluoranthene; 2,3,1′,8′-binaphthylene; dibenzo[bjk]fluorene
Benzo[ghi]perylene	191-24-2	DI6200500	1,12-benzoperylene
Benzo[a]pyrene	50-32-8	DJ3675000	3,4-benzopyrene; 6,7-benzopyrene
Chrysene	218-01-9	GC0700000	1.2-benzophenanthrene; benzo[a]phenanthrene
Dibenz[a,h]anthracene	53-70-3	HN2625000	1,2,5,6-dibenzanthracene
Fluoranthene	206-44-0	LL4025000	benzo[jk]fluorene; 1,2-benzacenaphthene; Idryl
Fluorene	86-73-7	LL5670000	o-biphenylenemethane; 2,2′-methylenebiphenyl; 9*H*-fluorene
Indeno[1,2,3-cd]pyrene	193-39-5	NK9300000	2,3-phenylenepyrene
Naphthalene	91-20-3	QJ0525000	Naphthene, naphthalin
Phenanthrene	85-01-8	SF7175000	Phenanthracene
Pyrene	129-00-0	UR2450000	benzo[def]phenanthrene

(1) Registry of Toxic Effects of Chemical Substances [6].
(2) Alternate names taken from Merck Index [7] and PubChem [10].

Table 2. Formulae and Physical Properties [1]

Compound (by MW)	Empirical Formula	Molecular Weight	Melting Point °C [2]	Boiling point °C [2]	Vapor Pressure mm Hg [3]	log P [4]
Naphthalene	$C_{10}H_8$	128.17	80.2	218	0.085	3.30
Acenaphthylene	$C_{12}H_8$	152.19	92.5	280	0.0048	3.94
Acenaphthene	$C_{12}H_{10}$	154.21	95	279	0.0025	3.92
Fluorene	$C_{13}H_{10}$	166.22	116	295	0.00842	3.77
Anthracene	$C_{14}H_{10}$	178.23	218	342	2.67E-06	4.45
Phenanthrene	$C_{14}H_{10}$	178.23	100	340	0.000112	4.46
Fluoranthene	$C_{16}H_{10}$	202.26	110	384	9.22E-06	5.16
Pyrene	$C_{16}H_{10}$	202.26	156	404	4.5E-06	4.88
Benz[a]anthracene	$C_{18}H_{12}$	228.29	155-157	435	1.9E-06	5.76
Chrysene	$C_{18}H_{12}$	228.29	254	448	6.23E-09	5.81
Benzo[b]fluoranthene	$C_{20}H_{12}$	252.32	168	481	5E-07	5.78
Benzo[k]fluoranthene	$C_{20}H_{12}$	252.32	217	480	9.65E-010	6.11
Benzo[a]pyrene	$C_{20}H_{12}$	252.32	179	312	5.49E-09	6.13
Benzo[ghi]perylene	$C_{22}H_{12}$	276.34	278	550	1E-010	6.63
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276.34	161.5-163	530	1.25E-010	6.70
Dibenz[a,h]anthracene	$C_{22}H_{14}$	278.35	266	524	1E-010 (@ 20 °C)	6.65

(1) Values Merck Index [7] and PubChem [10].
(2) Many of these compounds will sublime.
(3) Vapor pressure at 25 ^{o}C [5].
(4) Octanol-water partition coefficient [5].

Table 3. Exposure Limits[1, 2, 3]

Compound (alphabetically)	OSHA PEL	NIOSH REL
Acenaphthene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Acenaphthylene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Anthracene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Benz[a]anthracene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Benzo[b]fluoranthene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Benzo[k]fluoranthene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Benzo[ghi]perylene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Benzo[a]pyrene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Chrysene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Dibenz[a,h]anthracene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Fluoranthene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Fluorene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Indeno[1,2,3-cd]pyrene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Naphthalene	10 ppm (50 mg/m^3)	10 ppm (50 mg/m^3); STEL 15 ppm (75 mg/m^3)
Phenanthrene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)
Pyrene	0.2 mg/m^3 (benzene soluble fraction)	0.1 mg/m^3 (cyclohexane soluble fraction)

(1) OSHA Recommendations for Occupational Safety and Health [10].
(2) NIOSH Recommendations for Occupational Safety and Health [10].
(3) STEL = short term exposure limit [10].

Table 4. Approximate PAH Retention Times [(1)]

Compound (by elution order)	Approximate Retention Time (minutes)
Naphthalene-D_8	6.26
Naphthalene	6.28
Acenaphthylene	8.74
Acenaphthene-D_{10}	9.02
Acenaphthene	9.04
Fluorene	9.95
Phenanthrene-D_{10}	11.65
Phenanthrene	11.69
Anthracene	11.79
Fluoranthene	13.82
Pyrene	14.17
Benz[a]anthracene	15.90
Chrysene-D_{12}	15.92
Chrysene	15.96
Benzo[b]fluoranthene	17.83
Benzo[k]fluoranthene	17.89
Benzo[a]pyrene	18.58
Perylene-D_{12}	18.70
Indeno[1,2,3-cd]pyrene	21.95
Dibenz[a,h]anthracene	22.04
Benzo[ghi]perylene	22.95

(1) Actual retention times will vary with individual columns and column age.

Table 5. Mass Spectrometer Parameters for SIM operation [(1)]

	Start Time (minutes)	Dwell Time (ms)	Ions (*m/z*) 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

(1) These parameters monitor several ions for each PAH, which increases the certainty of the identification with minimal, if any, sacrifice of sensitivity.

Table 6. Quantitation Ions and Internal Standard References[(1)]

Compound (by elution order)	Quantitation ion (*m/z*)	Secondary Ions (*m/z*)	Internal Standard Reference
Naphthalene-D8	136	n/a	n/a
Naphthalene	128	129, 126, 64	Naphthalene-D_8
Acenaphthylene	152	153, 150, 76	Acenaphthene-D_{10}
Acenaphthene-D10	164	n/a	n/a
Acenaphthene	153	154, 152, 150, 76	Acenaphthene-D_{10}
Fluorene	166	167, 165, 164, 82	Acenaphthene-D_{10}
Phenanthrene- D10	188	n/a	n/a
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- D12	240	n/a	n/a
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}
Perylene- D12	264	n/a	n/a
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}

(1) Quantitation is performed using the single ion listed above as the quantitation ion. The secondary ions are included so that an abbreviated mass spectrum can be established for identity confirmation.

Table 7. Precision, Accuracy and Bias for 16 PAHs $(\bar{S}_{rT})$ [1,3]

Compound (alphabetically)	Range For Calculation[2] (µg/sample)	Bias (B)	Overall Precision $(\bar{S}_{rT})$	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	0.25 - 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) Backup Data Report [1]; with pump error correction

(2) 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.

(3) 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)

Table 8. Limits of Detection and Average Percent Recoveries by Concentration Level (µg/sample) [1,3]

Compound (alphabetically)	LOD[2]	Avg % Recovery at 0.25 (µg/sample)	Avg % Recovery at 0.75 (µg/sample)	Avg % Recovery at 2.50 (µg/sample)	Avg % Recovery at 7.50 (µg/sample)	Avg % Recovery at 25.0 (µg/sample)	Avg % Recovery at 75.0 (µg/sample)
Acenaphthene	0.08	97.1	92.6	96.1	87.6	93.8	83.8
Acenaphthylene	0.08	**64.7**	**71.0**	**57.9**	**67.5**	87.0	78.3
Anthracene	0.08	75.7	83.1	89.0	86.3	97.4	84.1
Benz[a]anthracene	0.08	86.7	86.1	94.7	92.1	103	86.4
Benzo[b]fluoranthene	0.08	92.8	91.6	95.7	91.7	104	87.4
Benzo[k]fluoranthene	0.1	83.0	86.3	101	91.0	97.5	86.7
Benzo[ghi]perylene	0.08	87.9	86.0	104	102	109	91.7
Benzo[a]pyrene	0.1	**70.1**	76.5	85.8	87.4	103	85.1
Chrysene	0.08	96.9	92.5	99.7	86.4	94.3	85.3
Dibenz[a,h]anthracene	0.1	86.7	87.3	105	102	109	89.0
Fluoranthene	0.08	95.1	92.6	97.8	91.9	105	87.4
Fluorene	0.08	95.7	92.3	98.2	90.8	97.4	85.0
Indeno[1,2,3-cd]pyrene	0.2	80.5	81.4	86.1	90.9	103	91.0
Naphthalene	0.1	110	96.3	101	87.6	95.1	85.7
Phenanthrene	0.08	97.1	92.3	99.6	90.1	98.6	86.3
Pyrene	0.08	92.3	91.4	92.7	89.3	99.1	86.2

(1) Backup Data Report [1]

(2) Limit of Detection in µg/sample determined from calibration curve using the method of Burkart [4]. Average percent recovery for seven replicates at each concentration level.

(3) Recoveries less than 75% are in bold text. Data from those levels were not used in accuracy, precision and bias calculations found in Table 7.

The data presented in Table 9 is from the user check and does not contain a correction for pump error. It is therefore S_r. This experiment was run at a different time by a different lab than the data presented in Table 7. The samples were spiked at different ranges and as a liquid injection with no air pulled through.

Table 9. Method Bias, Accuracy and Precision $(\overline{S}_r)$ [1,2]

Compound (alphabetically)	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
Benz[a]anthracene	0.5-20	-0.207	0.095	0.363	0.431
Benzo[b]fluoranthene	0.5-20	-0.207	0.080	0.338	0.395
Benzo[k]fluoranthene	0.5-20	-0.042	0.062	0.144	0.188
Benzo[ghi]perylene	0.5-20	-0.018	0.062	0.127	0.172
Benzo[a]pyrene	2-20	-0.141	0.081	0.273	0.343
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) These data are from the user check performed after method development.
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.

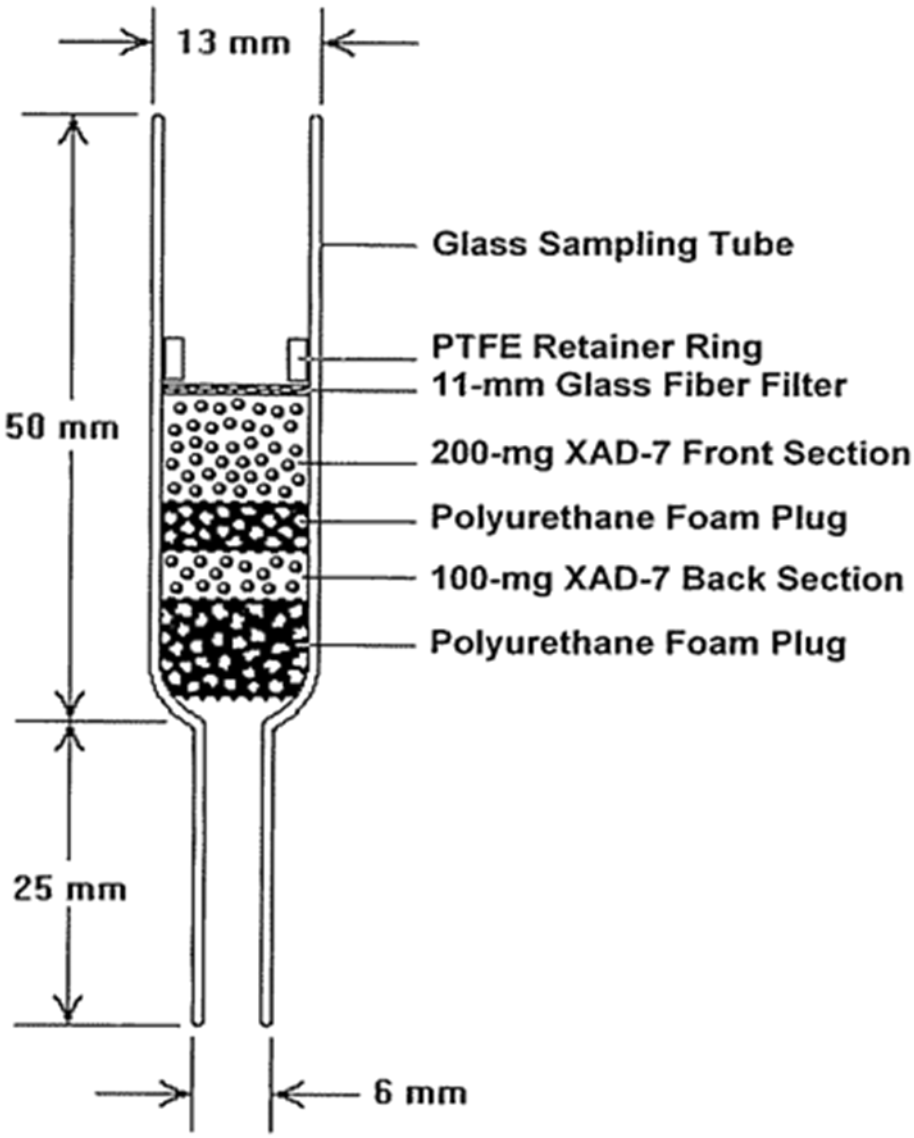

Figure 1. OVS-7 Sampler

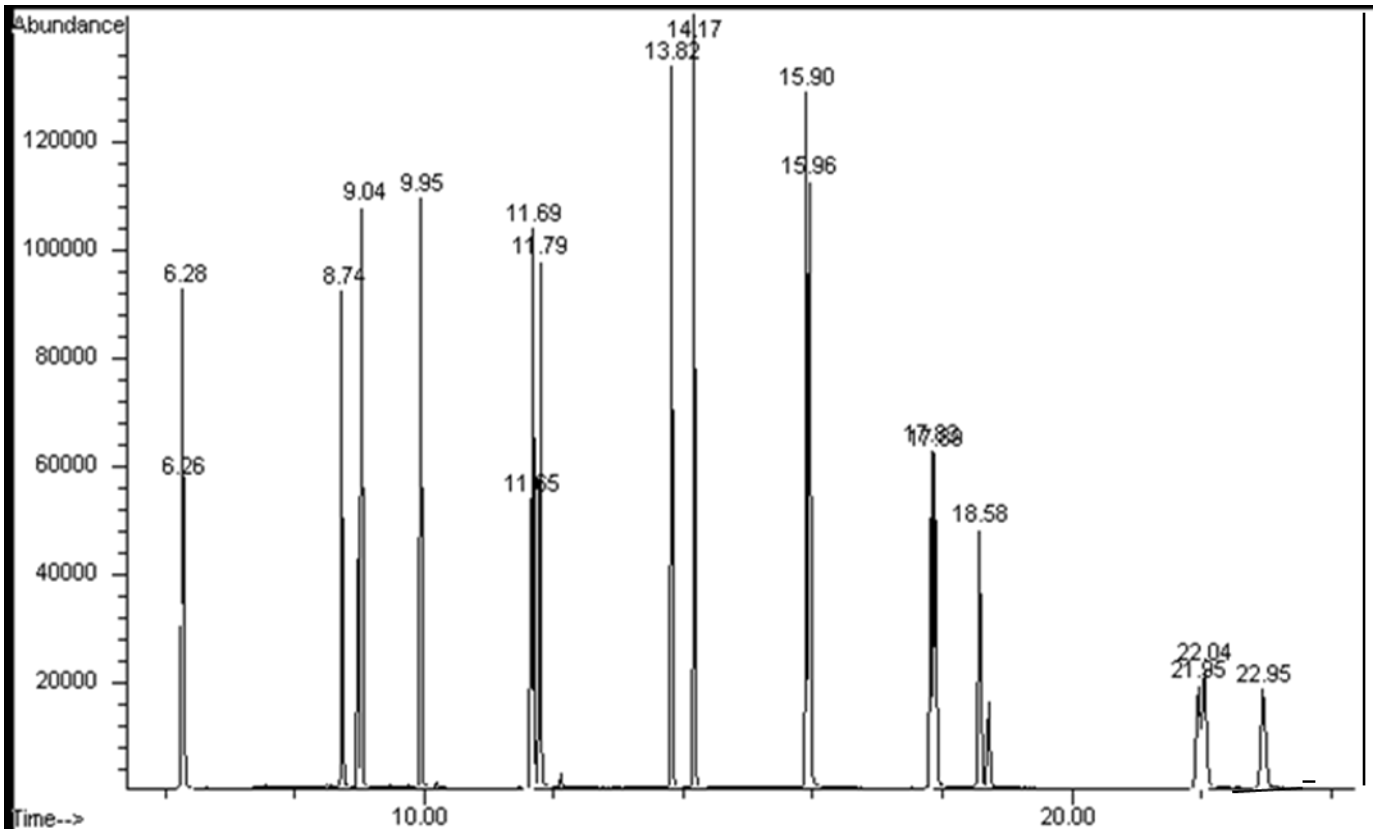

Figure 2. Sample Chromatogram. Identification of GC peaks is given in Table 4 by retention time.