A STUDY OF COAL LIQUEFACTION AND GASIFICATION PLANTS: AN INDUSTRIAL HYGIENE ASSESSMENT, A CONTROL TECHNOLOGY ASSESSMENT, AND THE DEVELOPMENT OF SAMPLING AND ANALYTICAL TECHNIQUES.

VOLUME IV

A METHOD FOR SAMPLING AND ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS IN COAL CONVERSION PLANTS AND PETROLEUM REFINERIES

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15. Supplementary Notes

16. Abstract (Limit: 200 words)

Methods of sampling and analysis of polynuclear aromatic (PNA) compounds used in industrial hygiene studies of coal liquefaction and gasification facilities were described. Personal and area air samples were collected in cassettes containing 200 milligrams or 25 grams, respectively, of Chromosorb 102. Flow rates during area sampling were 2.5 to 3.0 liters per minute and during personal sampling, 1.5 liter per minute. After collection, the samples were extracted with 300 milliliters (ml) of a methylene-chloride/methanol mixture in a Soxhlet apparatus. The extracts were reduced to a volume of 10ml, filtered, and concentrated to a volume of approximately 1ml. Aliquots, approximately 200 microliters, were analyzed with a gas chromatograph interfaced to a mass spectrometer. Some samples were stored at minus 20 degrees-C for up to 30 days before analysis. The precision of the method was determined by analyzing samples spiked with 11 PNA. Stability of the samples was not significantly affected by storage up to 30 days. Relative standard deviations of the spiked samples ranged from 11.0 percent for 100 nanograms (ng) of 2-methylphenanthrene (2531842) to 66.7 percent for 10ng of dibenz(a,i)pyrene (189559).

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DISCLAIMER

THE SAMPLING AND ANALYTICAL METHODS CONTAINED IN THIS DOCUMENT ARE NOT ENDORSED BY THE NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH (NIOSH). THE METHODS RELATED HERE ARE PRESENTED FOR PURELY INFORMATIONAL PURPOSES, SINCE THEY WERE USED IN THIS STUDY. SAMPLING AND ANALYSIS METHODS FOR PNA COMPOUNDS HAVE BEEN DEVELOPED BY THE DIVISION OF PHYSICAL SCIENCES AND ENGINEERING SINCE THIS STUDY WAS COMPLETED.

faction plants and petroleum refineries, conducted by the Enviro Control Division of the Dynamac Corporation for the National Institute for Occupational Safety and Health (NIOSH) (NIOSH Contract Nos. 210-78-0040, 210-78-0101, and 210-78-0082). As part of these studies, a validation study of the sampling and analytical protocols for polynuclear aromatic hydrocarbons (PNAs) was conducted under subcontract by the University of Iowa's University Hygienic Laboratory.

This volume is a companion document to the reports prepared under the referenced studies [1-3]. Since it may be of interest to individuals or groups involved in the analysis of PNAs in other occupational environments, it is published as a separate document.

One principal goal in each of the industrial hygiene studies was to quantitate exposure of workers in these industries to specific PNAs, particularly those known to be or suspected of being human carcinogens. To accomplish this, it was necessary to utilize a sampling method that would collect both light and heavy molecular weight PNAs and also be adaptable for personal sampling devices.

The traditional method of using the benzene-soluble fraction as an indicator of PNA exposures had several major drawbacks which precluded its utility in each of these studies, namely:

- nonspecificity,
- low sensitivity, and
- no relationship to actual concentrations of PNAs.

polymer solid sorbent, Chromosorb 102 (C-102). The backup bed of C-102 was required for trapping light molecular weight PNAs which are subject to losses from the silver-membrane filter. This configuration was successfully used for collection of area and personal samples throughout the course of the three industrial hygiene studies [1-3].

The present document describes in detail the sampling and analytical methods used for collection of PNAs in the three industrial hygiene studies, and the special study conducted to validate the sampling train.

trial hygiene studies in coal gasification and coal liquefaction plants [1,2]. The same protocols were subsequently used in a NIOSH-sponsored industrial hygiene study in nine petroleum refineries [3]. Two criteria were essential for the sampling method which was ultimately selected: (1) the device had to be suitable for conducting personal sampling, and (2) the device had to be capable of capturing both vapor-phase and particulate-phase PNAs.

Two configurations of the sampling assembly were used to collect particulate- and vapor-phase PNAs (Figures 1 and 2). The area sampling assembly contained approximately 2.5 grams of Chromosorb 102 (C-102), and the personal sampling assembly contained 200 milligrams (mg) in the glass tube. The larger mass of C-102 in the area sampler was used to prevent breakthrough of the samples since larger masses of PNAs were expected to be collected in the area samples than in personal samples.

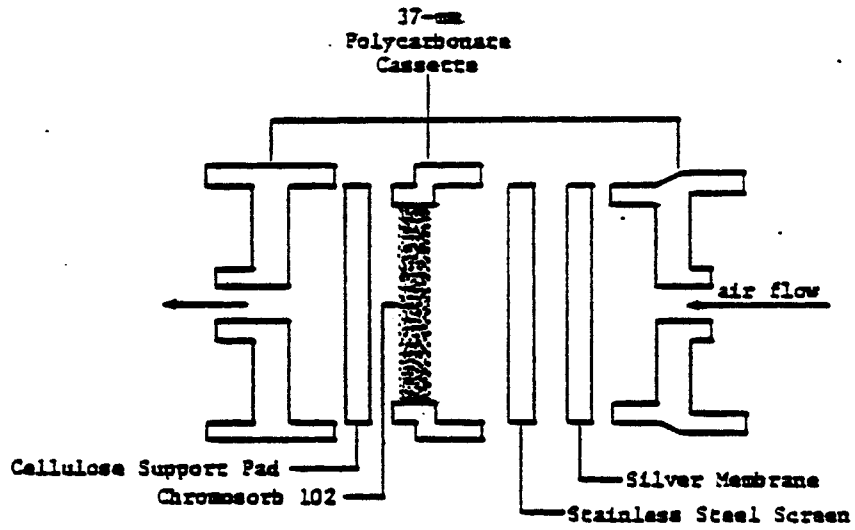

Figure 1. Area Sampling Device for PNAs

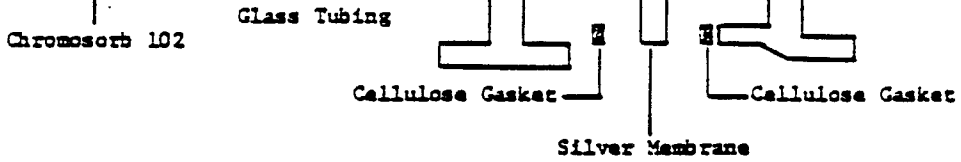

Figure 2. Personal Sampling Device for PNAs

A preliminary breakthrough study was conducted with acenaphthene using the dynamic U-tube method [5,6] to obtain an estimate of losses over a standard 8-hour sampling period. In the breakthrough study for the high-volume area sampler (containing approximately 2.5 grams of C-102), 20 mg of acenaphthene was injected into the U-tube flow chamber; the volume of air sampled was 2,000 liters (ℓ), and the sampling period was about 4 hours.

For the personal sampler (containing 200 mg of C-102), 0.5 mg of acenaphthene was injected into the U-tube system; air sample volumes were about 360 liters for a 4-hour sampling period. The results obtained indicated that there was no breakthrough for either device under the test conditions described; sample recovery was essentially 100 percent.

Chromosorb 102 -- purchased in bulk lots from Supelco, Inc. — was found to contain trace contaminants which interfered with PNA analysis. A cleanup protocol was developed to remove the contaminants, and all lots of C-102 were preextracted prior to assembling the PNA sampling devices. The cleanup protocol is presented in Table 1.

Methylene chloride/ Methanol (1:1, v/v)	2	48

The extracted C-102 was dried with a nitrogen stream filtered through a molecular sieve/carbon trap. The sampling devices were hand-assembled and sealed with shrink-bands.

Area and personal sampling was performed with either MSA or Bendix personal sampling pumps. Flow rates for the area samples were from 2.5 to 3.0 liters per minute (ℓpm). Sampling rates with the personal sampling devices were approximately 1.5 ℓpm.

Extraction of PNAs from the area sampler was as follows: the C-102 adsorbant and stainless steel backup screen were placed in a foil-wrapped soxhlet extractor fitted with a 500-milliliter (mℓ) round-bottom flask, and extracted with 300 mℓ of glass-distilled methylene chloride/methanol (1:1, v/v) for 22 hours. The extract was concentrated to approximately 10 mℓ in the round-bottom flash fitted with a 3-ball Snyder column. The concentrate was filtered through a Millipore sample clarifier (0.45-micrometer (μm) Teflon filter) into a 15-mℓ screwcap centrifuge tube. The extract was further concentrated in a Kontes heating block, regulated at 35°C under a stream of purified nitrogen. When approximately 1 mℓ in volume, the concentrate was quantitatively transferred to a 2-mℓ serum vial, fitted with a Teflon-lined rubber septum and crimp cap, and stored at -20°C in the dark until analysis.

The extraction procedure used for the silver-membrane filter was a modification of the NIOSH-validated Method No. P&CAM 217 [7]. The modifications

freezer at -20°C. Figure 3 shows a schematic of the extraction and concentration steps. If separate analysis of the C-102 and silver-membrane fractions was desired, they were not recombined in the final step.

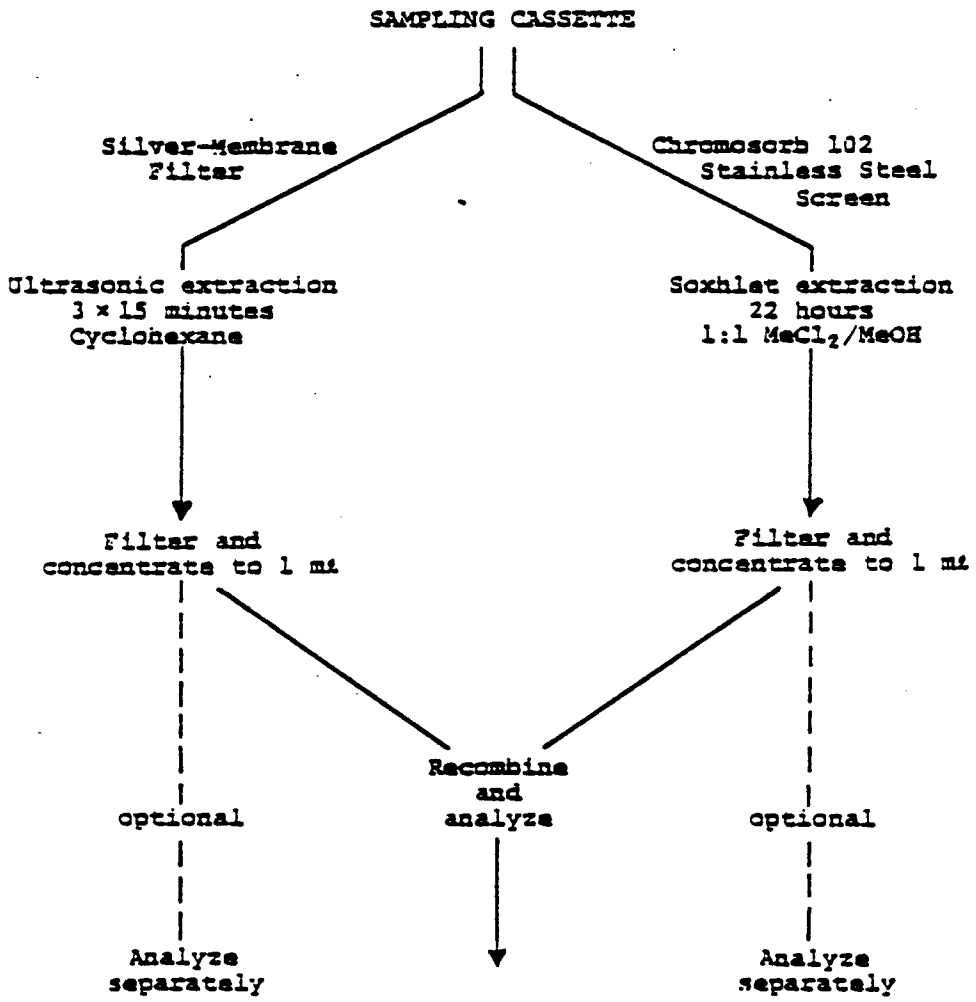

Figure 3. Sample Preparation Procedure

The extracts were analyzed on a Finnigan Model 4023 Gas [illegible] Spectrometer (GC/MS) that includes the 2300 Data General computer system. A glass jet separator was used as the interface. Electron impact spectra are obtained in a repetitive scanning mode. Operating conditions are summarized below:

- *GC Column:* 6 ft x 0.079-in i.d. glass column packed with 3% OV-17 80/100 mesh Supelcoport
- *Injector Temperature:* 260°C
- *GC/MS Interface Temperature:* 300°C
- *Transfer Line Temperature:* 280°C
- *MS Ionizer Block Temperature:* 300°C
- *Carrier Gas (Helium) Flow Rate:* 10 mℓ/min
- *Initial Temperature:* 50°C; held 4 minutes
- *Programmed Temperature:* 8°C/min
- *Final Temperature:* 260°C; held 50 minutes
- *MS Electron Multiplier Voltage:* 1800 V
- *MS Electron Energy:* 70 eV
- *MS Emission Current:* 500 mA

Columns were conditioned at 300°C for 48 hours. The MS is scanned from 40 to 350 AMU/second. The accelerating voltage is 3.5 kV, the emission current is 500 mA, and the electron energy is 70 eV. The MS is calibrated with perfluorotributylamine with a calibration range from 69 to 614 AMU. Masses are assigned to the computer using a least-squares analysis to an error of less than 150 millimass units. The mass spectrum is stable to ±0.05 AMU or better over an 8-hour period.

and the extracted ion used to quantitate the individual compounds found within the elution time window. Figure 4 is a sample chromatogram of an extract of the C-102 section from an area sampling device.

Table 2. Parameters Used for Identification of PNAs

Compound	M/E[a]	Relative Retention Time (6 replicates)
1. Naphthalene	128	0.527 ± 0.005
2. Quinoline	129	0.611 ± 0.004
3. 2-Methylnaphthalene	142	0.616 ± 0.005
4. 1-Methylnaphthalene	142	0.634 ± 0.003
5. Acenaphthalene	152	0.757 ± 0.002
6. Acenaphthene	154	0.780 ± 0.003
7. Fluorene	166	0.854 ± 0.007
8. Phenanthrene/Anthracene	178	1.001 ± 0.005
d_{10}-Anthracene	188	1.000
9. Acridine	179	1.026 ± 0.005
10. Carbazole	167	1.062 ± 0.003
11. Fluoranthene	202	1.172 ± 0.003
12. Pyrene	202	1.206 ± 0.002
13. Benzofluorene	216	1.268 ± 0.003
14. Benz(a)anthracene/Chrysene/Triphenylene	228	1.397 ± 0.004
15. Benzo(e)pyrene/Benzo(a)pyrene	252	1.610 ± 0.009
16. Perylene	252	1.629 ± 0.009
17. Dibenz(a,j)acridine	279	1.838 ± 0.139
18. Dibenz(a,i)carbazole	267	1.891 ± 0.029
19. Indeno(1,2,3-cd)pyrene	276	1.918 ± 0.033
20. Dibenzanthracene	278	1.927 ± 0.034
21. Benzo(g,h,i)perylene	276	2.017 ± 0.037
22. Coronene	300	2.964 ± 0.106
23. Dibenzpyrene	302	3.176 ± 0.099

[a]Mass/Charge.

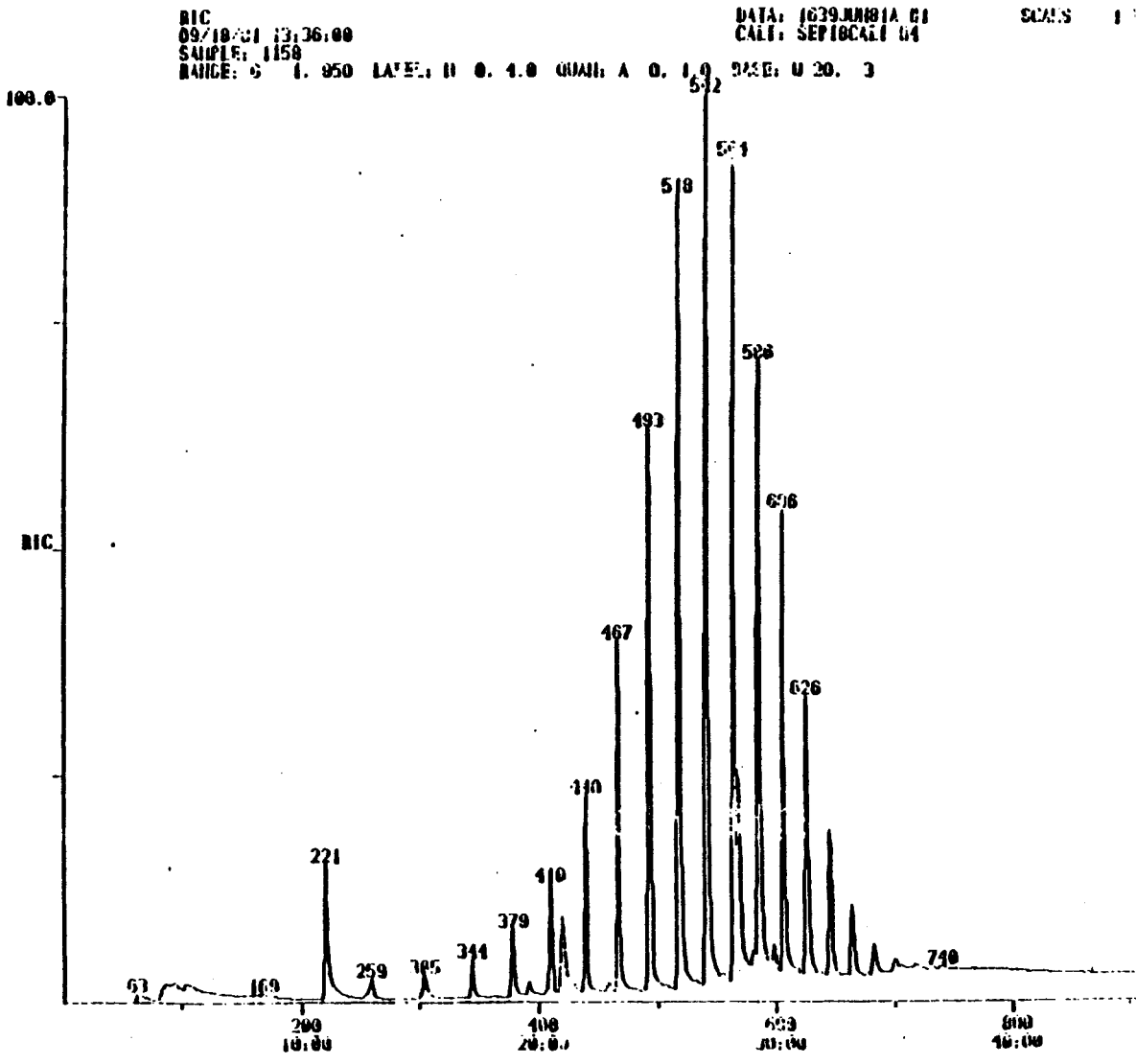

Figure 4. Sample Chromatogram

The GC/MS analysis of a PNA mixture reported by Lao et al. [8] could not be reproduced. The GC parameters used for the fractionation and quantitation of the PNA reference compounds were:

- *GC Column:* 12 ft x 0.125-in i.d. stainless steel packed with 6% Dexsil 300 on 80/100 mesh Chromosorb W (HP) (purchased from Applied Science)
- *Sample Injector Temperature:* 325°C
- *GC/MS Interface Temperature:* 325°C
- *Carrier Gas (Helium) Flow Rate:* 40 mℓ/min
- *Initial Temperature:* 165°C; held for 2 minutes
- *Programmed Temperature:* 4°C/min to 295°C

  Final Temperature: 295°C; held for 50 minutes

Problems encountered include excessive bleeding of the 6% Dexsil 300 column, even after conditioning it for 6 days at 375°C. Such bleeding completely masks peaks having retention times greater than triphenylene (retention time 29 minutes). Anomalous peaks showed on the MS, which are due to breakdown products from the GC injection port septum at the operational injector temperature of 325°C, thus further masking high retention peaks. Septa of various materials, including silicone, were used, but all gave unsuccessful results.

GC/MS with Nematic Liquid-Crystal Stationary Phase

Separation of the reference PNA hydrocarbons can also be accomplished by using a GC column packed with a nematic liquid-crystal stationary phase: ',N'-bis(p-phenylbenzylidine)-α,α'-bis(p-toluidine) [9]. The GC parameters ed were:

The GC analysis of the PNA reference samples was accomplished; however, the lack of adequate sensitivity makes this method less desirable than that with OV-17 described previously.

tainers specially designed for the shipment of materials under refrigeration. Filters, impinger liquids, charcoal and silica gel tube samples, and bulk samples were packed in separate containers to prevent breakage and contamination.

All samples were shipped to the laboratory at the completion of the sampling program by overnight express delivery service.

The procedures followed by the laboratory upon receipt of the samples were as follows:

- Containers were examined to ensure integrity of each sample. Lab numbers were assigned for each sample and logged in.
- The 'request for analysis' sheets (field data sheets) were placed in an 'Analytical Request' binder. Aqueous samples were labeled and placed in a walk-in cooler; nonaqueous samples were labeled and placed in a freezer at -20°C.
- Each series of samples was analyzed in the order in which it was received by the laboratory. No other samples were analyzed until previous analytical work had been completed.
- A report was prepared including the following:
  - field data sheet - completed
  - sample preparation protocol
  - blank preparation protocol
  - calculations and/or information from standard or known analytical analyses
  - reagent blank and desorption correction factors.

Instrument calibrations were performed with pure standards at least once a day for the mass spectrometer and routinely in the course of sample analysis

PNAs	
Naphthalene	Fisher
2-Methylnaphthalene	EPA
1-Methylnaphthalene	EPA
Acenaphthalene	Eastman
Acenaphthene	Eastman
Anthracene	Aldrich
Phenathrene	Aldrich
Fluorene	Pfaltz & Bauer
Pyrene	Eastman
Fluoranthene	Aldrich
Benz(a)anthracene	Pfaltz & Bauer
Benzo(a)fluorene	ICN
Benzo(b)fluorene	ICN
7,12-Dimethylbenz(a)anthracene	Fisher/Sargent Welch
Dibenz(a,c)anthracene	ICN
Dibenz(a,h)anthracene	ICN
Perylene	Tridon
Naphthacene	Fisher/Sargent Welch
Benzo(e)pyrene	Eastman
Benzo(a)pyrene	Eastman
Dibenzo(a,h)pyrene	Pfaltz & Bauer
Dibenzo(a,i)pyrene	Sigma
Chrysene	Aldrich
Coronene	Aldrich
Triphenylene	Tridom
Aza-PNAs	
Dibenz(a,j)acridine	Sigma
Dibenz(a,i)carbazole	Aldrich
Carbazole	Aldrich
Acridine	Aldrich
Quinoline	EPA

- PNAs quantitated by the internal standard d_{10}-anthracene.
- Solvent blanks analyzed with each series or each new lot of solvent (1/35 samples).
- Replicates analyzed with each series (1/15 samples).
- Field blanks spiked with standard mixtures of PNAs (1/20 samples).
- Spikes with selected PNAs analyzed with each series (1/20 samples).
- All samples extracted within 14 working days, placed in Teflon-lined crimp top vials, and analyzed within 45 days.
- Logs maintained on extraction apparatus including such information as dates samples extracted, sample number, apparatus number, and other comments.

variables were:

- efficiency of Chromosorb 102 (C-102) as a solid adsorbant for trapping and retaining vapor-phase polynuclear aromatic hydrocarbons (PNAs);
- chemical stability of PNAs on the sorbent, once trapped;
- ability to quantitatively extract trapped PNAs; and
- reproducibility (precision) and sensitivity of the combined sampling and analytical methods.

For this assessment, a multiphase study was designed and executed by the University Hygienic Laboratory (UHL), University of Iowa, under contract to Enviro Control, Inc. (now Dynamac Corporation). Eight discrete phases were identified:

1. Characterization of preexisting contaminants on commercial C-102.

2. Determination of breakthrough volumes for representative species of PNAs.

3. Determination of optimum extraction solvents and procedures for PNAs.

4. Quantitation of desorption efficiencies for PNAs from C-102.

5. Evaluation of stability of PNAs on C-102.

6. Quantitation of variability (precision) of sample injection and GC/MS instrument response.

industrial hygiene studies.

Table 4. Representative PNAs Used in the Sampling Train Validation Study

Compound	Number of Rings	Molecular Weight
1-Methylnaphthalene	2	142.20
Phenanthrene	3	178.22
Carbazole	3	167.21
2-Methylphenanthrene	3	192.22
Pyrene	4	202.24
Triphenylene	4	228.28
Benzo(k)fluoranthene	4	252.32
Benzo(a)pyrene	5	252.32
Dibenzo(a,i)carbazole	5	267.00
Dibenz(a,c)anthracene	5	278.33
Dibenzo(a,i)pyrene	6	302.28

investigations of what procedure was necessary to remove these contaminants.

Only carbazole and 2-methylphenanthrene, in amounts of roughly 126 micrograms (μg) and 2.3 μg, respectively, were found on the silver-membrane filter. Ultrasonic extraction to clean the filter was carried out for 15 minutes at 200 watts using 5 milliliters (mℓ) of cyclohexane. Afterwards, neither of these PNA compounds appeared in the solvent used for a second extraction with a detection level of 0.25 to 1 nanogram (ng) (depending on the compound), nor in the solvent used for a third and final extraction. Thus, a single ultrasonic extraction of the silver-membrane for 15 minutes with 5 mℓ of cyclohexane was sufficient to remove any PNA interferences.

For Chromosorb 102, the picture was considerably more complex. Table 5 summarizes the results of the cleanup procedure used to remove interferences prior to use of the solid sorbent. A mass of 150 grams (g) of C-102 was extracted with successive volumes of 1,500 mℓ of 1:1 methylene chloride/methanol. As Table 5 indicates, none of the 12 representative compounds identified in the initial extract appeared in the extracting solution subsequent to the fifth extraction. This suggests that five or, at most, six extractions of the C-102 suffice to remove all of the potential interferences. It should be noted that approximately 300 different peaks were observed in the first C-102 extract, using capillary gas chromatography, with retention times ranging from 0.32 to 33.89 minutes (the indicator compounds ranged in retention time from 7.56 to 32.78 minutes), and a total integrator area of $\sim 9.36 \times 10^6$. The eighth extraction had a total of 46 different peaks, none of which masked peaks of the 12 PNAs, with a total integrator area of $\sim 3.43 \times 10^4$. No effort was made to identify or quantitate compounds other than the 12 of interest.

Table 5. Analysis of Contaminants[a] on 150 Grams of Chromosorb 1

Compound[b]	Extraction Number							
	1[a]	2[a]	3[a]	4[c]	5[d]	6[d]	7[e]	8[e]
2-Methylnaphthalene	202	9.6	3.3	0.94	0.084	<0.25	<0.25	<0.25
1-Methylnaphthalene	? <6.2	102 ?	2.9	0.87	0.087	<0.25	<0.25	<0.25
Phenanthrene	187	<0.25	4.5	0.32	<0.23	<0.25	<0.25	<0.25
Carbazole	2,170	78.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2-Methylphenanthrene	689	<0.25	2.3	<0.25	0.16	<0.25	<0.25	<0.25
Pyrene	<6.2	<0.25	2.0	0.35	0.088	<0.25	<0.25	<0.25
Triphenylene	399	4.8	1.2	<0.25	0.99	<0.25	<0.25	<0.25
Benzo(k)fluoranthene	? <12.5	334 ?	22.4	1.8	1.1	<0.5	<0.5	<0.5
Benzo(a)pyrene	? <12.5	657 ?	6.5	<0.5	0.22	<0.5	<0.5	<0.5
13H-Dibenzo(a,i)carbazole	606	57.0	11.9	<1	0.40	<1	<1	<1
Dibenz(a,c)anthracene	131	18.3	1.2	0.47	0.27	<0.25	<0.25	<0.25
Dibenzo(a,i)pyrene	171	23.8	4.7	<1	<1	<1	<1	<1
TOTAL (µg)	4,555	1,285	62.9	4.75	3.63	<5.25	<5.25	<5.25

[a]All numbers are total micrograms of the contaminant removed from the C-102 during the particular e

[b]All data from capillary gas chromatography; compound identities based on retention time.

[c]Refluxing for 12 hours each with methylene chloride. [d]Refluxing for 12 hours each with meth

[e]Refluxing for 12 hours each with 1:1 methylene chloride/methanol.

ture. These data are summarized in the last column of Table 5.

Phase 2. Determination of Breakthrough Volumes

In order to determine whether or not the capacity of the two-stage sampling cassette used to trap PNAs would be exceeded during sampling, experiments were set up to determine if breakthrough volumes for the PNAs were exceeded with the approximate air sample volumes used in the industrial hygiene studies. In order to do this, approximately 20 µg of each of the PNAs studied (except 1-methylnaphthalene which was approximately 500 µg) was loaded onto the silver-membrane filter surface of a two-stage sampler of the configuration used for high-volume, area sampling (Figure 1).

Attached to the outlet of the cassette was a tube containing 150 mg of clean C-102. The presence of any PNAs in this 'tail' tube would indicate that breakthrough had occurred. A manifold was set up with six identical devices attached including four identical spiked samplers and two blank samplers. A needle valve was connected upstream of each sampling cassette in order to regulate air flow, and two Greenberg-Smith impingers with 250 mℓ of water in each were attached to the outlet of the Gast high-volume pump to scrub the exhaust, should it become contaminated. A total of 4,000 ℓ of air at 35°C (95°F) and 70 to 80% relative humidity was drawn through the cassette and tail tube at a rate of 9 liters per minute (ℓpm), with periodic replacement of the tail tubes.

cluded that the breakthrough volume for the 12 compounds, at the temperature and humidity described, is greater than 4,000 liters of air.

Phase 3. Determination of Optimum Extraction Procedures for PNAs

In order to determine the optimum extraction time for the silver-membrane filter and C-102 sections, 5 µg of each of 11 PNAs were spiked onto a silver-membrane filter. For the Chromosorb 102, between 5 and 10 µg of each of the compounds studied was loaded on the solid sorbent (only about 1.41 µg of dibenzo(a,i)carbazole was used).

The silver-membrane filter was extracted with 5 mℓ of cyclohexane, using an ultrasonic bath for 15 minutes, and the extracting solution was analyzed. The extraction was repeated twice more, and each time the extracting solution was analyzed for the 11 representative PNAs. No PNAs were found in the second or third extracting solution, indicating that essentially all of the PNAs will be removed during the first extraction with cyclohexane.

The C-102 was refluxed with five successive batches of 300 mℓ of methylene chloride/methanol (1:1). The first and second extractions were for 1 hour each, the third for 2 hours, the fourth for 4 hours, and the fifth for 8 hours.

Ninety-eight percent (98%) of the total mass of the compounds added to the C-102 was recovered after the first hour of extraction. Subsequent

Phase 4. Determination of Desorption Efficiencies

Desorption efficiencies were determined for the 11 representative PNAs from both the silver-membrane filter and the C-102. Three concentration levels (500, 5,000, and 50,000 ng) in six replicates each were loaded onto the silver-membrane filters and 3.5 grams of the C-102.

The silver-membrane filters were extracted ultrasonically with cyclohexane as previously described. The 15 mℓ of extract was concentrated to about 2 mℓ; then 4 mℓ of methanol was added and reduced to about 400 µℓ.

The Soxhlet thimbles containing the spiked C-102 were extracted in a Soxhlet for 16 hours with 300 mℓ of methylene chloride/methanol (1:1). The extracting solution was reduced to about 5 mℓ using a Snyder column and heating mantle. The extract was quantitatively filtered through a 0.45-µm Teflon filter and transferred to a micro-Snyder concentrator and reduced to 400 µℓ. The concentrate was quantitatively transferred to crimp-top vials prior to analysis by GC/MS.

Final volumes of concentrated desorbing solutions were adjusted just prior to analysis so that the mass of PNAs injected into the GC/MS for each sample was approximately the same.

Table 6 summarizes the desorption efficiencies determined for the silver-membrane filters and Table 7 shows the results for the C-102 along with standard deviations and relative standard deviations for the measurements. In general, the relative standard deviations decline as the mass of PNAs spiked increases.

Compound	Mean % Recovery[b]	S.D. (%)	R.S.D. (%)	Mean % Recovery[c]	S.D. (%)	R.S.D. (%)	Mean % Recovery[b]	S.D. (%)	R.S.D. (%)
1-Methylnaphthalene	12.0[d]	± 6.1	50.8	11.5[e]	± 4.7	40.9	76.2	± 17.0	22.3
Phenanthrene	81.8	± 17.7	21.6	94.9	± 10.1	10.6	80.8	± 4.3	5.4
Carbazole	58.0	± 16.7	28.8	53.0	± 17.7	33.4	98.0	± 7.7	7.9
2-Methylphenanthrene	86.5	± 7.2	8.3	101.6	± 22.9	22.5	84.3	± 7.2	8.6
Pyrene	84.8	± 14.7	17.3	117.4	± 16.5	14.0	72.2	± 7.1	9.8
Triphenylene	80.2	± 17.7	22.1	119.4	± 22.2	18.6	83.0	± 8.8	10.7
Benzo(k)fluoranthene	87.2	± 15.3	17.5	141.3	± 70.1	49.6	85.5	± 17.5	20.5
Benzo(a)pyrene	82.2	± 22.7	27.6	90.9	± 14.5	15.9	76.5	± 3.3	4.3
Dibenzo(a,i)carbazole	67.8[e]	± 29.2	43.1	74.6	± 23.2	31.1	81.3	± 10.1	12.4
Dibenz(a,c)anthracene	82.8	± 16.1	19.4	107.1	± 11.6	10.8	66.0	± 5.2	7.9
Dibenzo(a,i)pyrene	-[f]	-[f]	-[f]	58.6[e]	± 8.6	14.7	53.8	± 19.8	36.9

[a] All PNAs corrected by internal standards: d_{10}-anthracene for 1-methylnaphthalene through pyrene; d_{12}-chrysene for the remaining compounds.

[b] Means based on six measurements unless otherwise footnoted.

[c] Means based on seven measurements unless otherwise footnoted.

[d] Mean based on three measurements.

[e] Mean based on five measurements.

[f] Small peak heights and integrator areas prevented calculation of these values.

Compound	Mean % Recovery[b]	S.D. (%)	R.S.D. (%)	Mean % Recovery[b]	S.D. (%)	R.S.D. (%)	Mean % Recovery[b]	S.D. (%)	R.S.D. (%)
1-Methylnaphthalene	111.7	± 76.9	68.8	113.3	± 28.7	25.3	91.7	± 69.5	75.8
Phenanthrene	90.7	± 50.6	55.7	90.8	± 27.6	30.4	77.3	± 8.2	10.6
Carbazole	111.5	± 88.1	79.0	99.8	± 39.1	39.2	79.5	± 12.8	16.2
2-Methylphenanthrene	100.7	± 59.3	58.9	102.7	± 41.9	40.8	73.8	± 5.3	7.1
Pyrene	100.0	± 63.5	63.5	114.0	± 40.0	35.1	83.7	± 10.0	12.0
Triphenylene	104.7	± 32.2	30.8	94.2	± 9.9	10.5	58.0	± 10.7	18.5
Benzo(k)fluoranthene	143.3	± 74.5	52.0	113.7	± 48.0	42.2	51.2	± 22.9	44.7
Benzo(a)pyrene	126.7	± 57.5	45.4	104.8	± 23.0	21.9	74.0	± 20.1	27.2
Dibenzo(a,i)carbazole	156.7	± 102.3	65.3	131.7	± 73.1	55.5	95.8	± 25.6	26.8
Dibenz(a,c)anthracene	156.2	± 63.9	40.9	123.5	± 43.9	35.6	78.0	± 23.7	30.4
Dibenz(a,i)pyrene	-[c]	-[c]	-[c]	84.5	± 17.2	20.3[d]	46.7	± 25.1	53.8

[a] All PNAs corrected by internal standards: d_{10}-anthracene for 1-methylnaphthalene through pyrene; d_{12}-chrysene for the remaining compounds.

[b] All values based on six measurements unless otherwise footnoted.

[c] Small peak heights and integrator areas prevented calculation of these values.

[d] Value based on four measurements.

of four separate spikes.

Table 8. Desorption Efficiencies for Chromosorb 102 Conducted on Field Blanks

Compound	% Recovery	
	Lot 282[a]	Lot 293[a]
Naphthalene	41	39
1-Methylnaphthalene	48	50
2-Methylnaphthalene	48	49
Quinoline	72	81
Acenaphthalene	56	62
Acenaphthene	56	62
Fluorene	71	82
Phenanthrene/Anthracene	65	80
Acridine	65	69
Carbazole	89	102
Fluoranthene	77	93
Pyrene	79	98
Benzo(a)fluorene/Benzo(b)fluorene	93	100
Benz(a)anthracene/Chrysene/Triphenylene	76	90
Benzo(j)fluoranthene/Benzo(b)fluoranthene/Benzo(k)fluoranthene	87	110
Benzo(e)pyrene/Benzo(a)pyrene	78	87
Perylene	81	92
Dibenz(a,j)acridine	91	108
Dibenz(a,i)carbazole	88	91
Indeno(1,2,3-cd)pyrene	87	104
Dibenz(a,h)anthracene	92	104
Benzo(g,h,i)perylene	88	88
Coronene	108	110
Dibenz(a,i)pyrene	197	140
Dimethylbenz(a)anthracene	96	124
3-Methylcholanthrene	87	-[b]
6,13-Dimethyldibenz(a,h)anthracene	87	-[b]

[a] Average of four separate determinations.

[b] Not determined.

A series of experiments were carried out to determine the stability of the 11 representative PNAs on the two-stage sampling cassettes. Twelve two-stage cassettes were each spiked with approximately 10 µg each of the 11 representative compounds. Five µg of each compound were loaded onto the silver-membrane filter and the other 5 µg put directly onto the Chromosorb 102. Six of these samples were extracted 24 hours after preparation and then analyzed. The other six samples were stored in the dark at -20°C for 30 days before extraction and analysis. The percent recoveries, as well as the absolute standard deviations of these recoveries, for both the 1-day and the 30-day storage experiments are shown in Table 9.

Table 9. Recoveries of Representative Compounds From Two-Stage Cassettes As a Function of Storage Time

Compound	1-Day Storage Time		30-Day Storage Time	
	Mean % Recovery[a]	Standard Deviation (%)	Mean % Recovery[a]	Standard Deviation (%)
1-Methylnaphthalene	105	39	150	91
Phenanthrene	83	10	103	33
Carbazole	65	9	105	44
2-Methylphenanthrene	86	15	110	48
Pyrene	89	17	112	45
Triphenylene	67	30	45	26
Benzo(k)fluoranthene	69	32	47	24
Benzo(a)pyrene	61	29	41	24
Dibenzo(a,i)carbazole	58	28	50	30
Dibenz(a,c)anthracene	64	30	42	22
Dibenzo(a,i)pyrene	51	29	65	44

[a]Values based on measurements of six different samples.

Table 6 or Table 7. The data in Table 9 were produced by following the extraction scheme which combines the two solutions right after the initial extraction. The standard deviations of the measurements of recovery from the cassettes at 1 and 30 days are so large as to obscure any small-to-moderate changes in recovery that were sought in these experiments.

The high recoveries seen for 1-methylnaphthalene through pyrene for the 30-day study cannot be attributed to contamination. Reagent blanks were run with each set of experiments and all glassware was subjected to a scrupulous cleaning process before use.

Phase 6. Precision of Sample Injection and Instrument Response

This phase was included to evaluate all contributions to precision from filling the syringe through integration of a specific ion peak generated by the GC/MS system.

The measurements of the precision resulting from repetitive analyses of the same sample were done in the following way. Three standard solutions which contained four different concentrations of the 11 PNAs were prepared in methylene chloride. The concentrations in the solutions were such that the injection of a 2-µl sample into the GC/MS would give approximately 10, 30, 60, and 100 ng total mass of each of the compounds, respectively. The measurements of precision are all reported in terms of the variation of the relative response factor. The response factor (in MS) is the number of ions of a given M/E ratio counted per unit mass of the substance analyzed. The relative response factor is the ratio of the response

Approximately 125 ng of d_{10}-anthracene was in each 2-μl sample; the amount of d_{12}-chrysene in each 2-μl sample was at approximately the same level as that of the PNAs in the particular sample.

Table 10 summarizes the results of these measurements, which are intended to determine the uncertainties associated with repetitive injection and then quantitation of identical samples, at four different levels for each of the 11 PNA species. The relative standard deviations of these measurements range from 11.0% for 100 ng of 2-methylphenanthrene to 66.7% for 10 ng of dibenzo(a,i)pyrene.

The data reported in Table 10 show that the relative standard deviation of the measurements tends to decrease as the mass of material injected increases. Ten nanograms of PNA are just at the detection limit for these compounds, and since the relative response factor also tends to decline with increasing molecular weight, it is very difficult to quantitate the higher molecular weight compounds at low levels.

Pyrene	0.94	1.03	1.13	1.16	12.5	10.9	6.4	12.6
Triphenylene	1.71	1.51	1.32	1.29	14.1	7.7	5.8	5.8
Benzo(k)fluoranthene	1.07	0.71	0.70	0.70	18.6	11.1	24.7	13.6
Benzo(a)pyrene	0.80	0.56	0.57	0.58	22.3	23.8	21.7	14.0
Dibenzo(a,i)carbazole	0.46	0.37	0.34	0.47	29.5	39.6	25.0	22.7
Dibenz(a,c)anthracene	0.59	0.55	0.56	0.64	15.7	33.3	19.0	11.6
Dibenzo(a,i)pyrene	0.86	2.66[d]	2.02[d]	2.28	99.4	11.4	20.1	15.6

[a]Internal standards used for response factor normalization: d_{10}-anthracene for 1-methylnaphthalene through pyrene; d_{12}-chrysene for the remaining compounds.

[b]Relative response factor = (height/ng of compound)/(height/ng of internal standard).

[c]Based on six measurements at 10 ng and 100 ng, and on five measurements at 30 ng and 60 ng.

[d]Area data.

Phase 7. Results of Replicate Field Samples

An opportunity presented itself during the industrial hygiene surveys at nine petroleum refineries [3] to conduct replicate area sampling for PNAs. These samples were analyzed and summaries of the data are shown in Tables 11 and 12. The data in Table 11 are for the samples where PNA concentration ranges were found at levels of less than 0.50 $\mu g/m^3$. Table 12 shows the results of the replicate samples where PNA concentrations were greater than 0.50 $\mu g/m^3$. These data give an overview of the total uncertainty associated with all the steps for sampling and analysis of PNAs in the workplace environment: collection, shipping, storage, desorption, and analysis. The data thus incorporate not only the uncertainties studied in the validation of this particular sampling train, but also those intrinsic to co-location sampling itself.

1-Methylnaphthalene	0.19 - 0.44	2	10	8
Acenaphthalene	<0.01 - 0.41	16	122	84
Acenaphthene	0.01 - 0.32	12	73	68
Fluorene	0.01 - 0.35	12	68	74
Phenanthrene/Anthracene	0.02 - 0.42	12	71	73
Acridine	0.01 - 0.38	15	118	78
Carbazole	<0.01 - 0.48	16	90	74
Fluoranthene	<0.01 - 0.29	15	116	83
Pyrene	0.01 - 0.41	13	96	76
Benzofluorene	<0.01 - 0.43	9	144	68
Benz(a)anthracene/Chrysene/ Triphenylene	<0.01 - 0.46	13	118	82
Benzo(e)pyrene/Benzo(a)pyrene	0.01 - 0.39	6	130	81
Perylene	0.01 - 0.13	6	200	—
Dibenz(a,j)acridine	0.03 - 0.36	3	200	—
Dibenzo(a,i)carbazole	0.02 - 0.22	6	170	73
Indeno(1,2,3-cd)pyrene	0.04 - 0.33	2	200	—
Dibenzanthracene	0.04 - 0.44	2	200	—
Benzo(g,h,i)perylene	0.04 - 0.05	2	200	—

*Average relative range = $\frac{1}{N} \sum_{1}^{n} \left(\frac{X_A - X_B}{\frac{X_A + X_B}{2}} \cdot 100 \right)$

where X_A and X_B are the results for each of the pair of replicate samples.

Quinoline	0.88 - 3.99	5	48.2	37.8
1-Methylnaphthalene	0.79 - 30.73	11	37.3	30.9
2-Methylnaphthalene	0.51 - 25.74	10	40.8	36.4
Acenaphthene	1.05 - 7.55	4	53.6	51.6
Fluorene	0.97 - 6.19	4	55.5	62.9
Phenanthrene/Anthracene	3.39 - 23.35	4	59.4	62.5
Acridine	0.57 - 1.91	3	92.9	93.1
Fluoranthene	0.52 - 0.72	3	41.4	7.5
Pyrene	0.92 - 2.69	4	54.4	37.7

*Average relative range = $\frac{1}{N} \sum_{1}^{n} \left(\frac{X_A - X_B}{\frac{X_A + X_B}{2}} \cdot 100 \right)$

where X_A and X_B are the results for each of the pair of replicate samples.

quent ultrasonic extraction with cyclohexane. This method became the standard for industrial hygienists for collection of PNAs. An EPA assessment [10] concluded that no tetracyclic and larger PNAs were lost from glass fiber filters alone with 2 hours of sampling at 1.2 cubic meter/minute.

Since the industrial hygiene studies in the petroleum refining and coal conversion industries were attempting quantitation of PNA species of 2 and 3 rings in addition to the PNA species of 4 through 7 rings, the porous polymer solid sorbent Chromosorb 102 was used to trap the lighter molecular weight PNAs.

Sixty samples were analyzed for the cyclohexane-soluble fraction collected on the silver-membrane filter and the extracts subsequently analyzed by GC/MS for specific PNAs. Results of these data were combined with the PNAs found on the backup section of C-102 and compared with the cyclohexane-soluble fraction previously determined. Figures 5, 6, 7, and 8 show scattergrams of the results of these determinations and the correlation coefficients.

A statistical evaluation of the linear relationship between analytical determinations of the PNA (total of 34) concentrations ($\mu g/m^3$) and the benzene-soluble concentrations ($\mu g/m^3$) in the same air samples collected at coal liquefaction and gasification plants showed a very poor correlation of the two results. Using logarithmic values of these concentrations did not significantly alter the correlations. Similarly, evaluating the linear relationship between the total of PNAs having more than 2 rings and the benzene-soluble concentrations of the samples did not significantly alter the correlation.

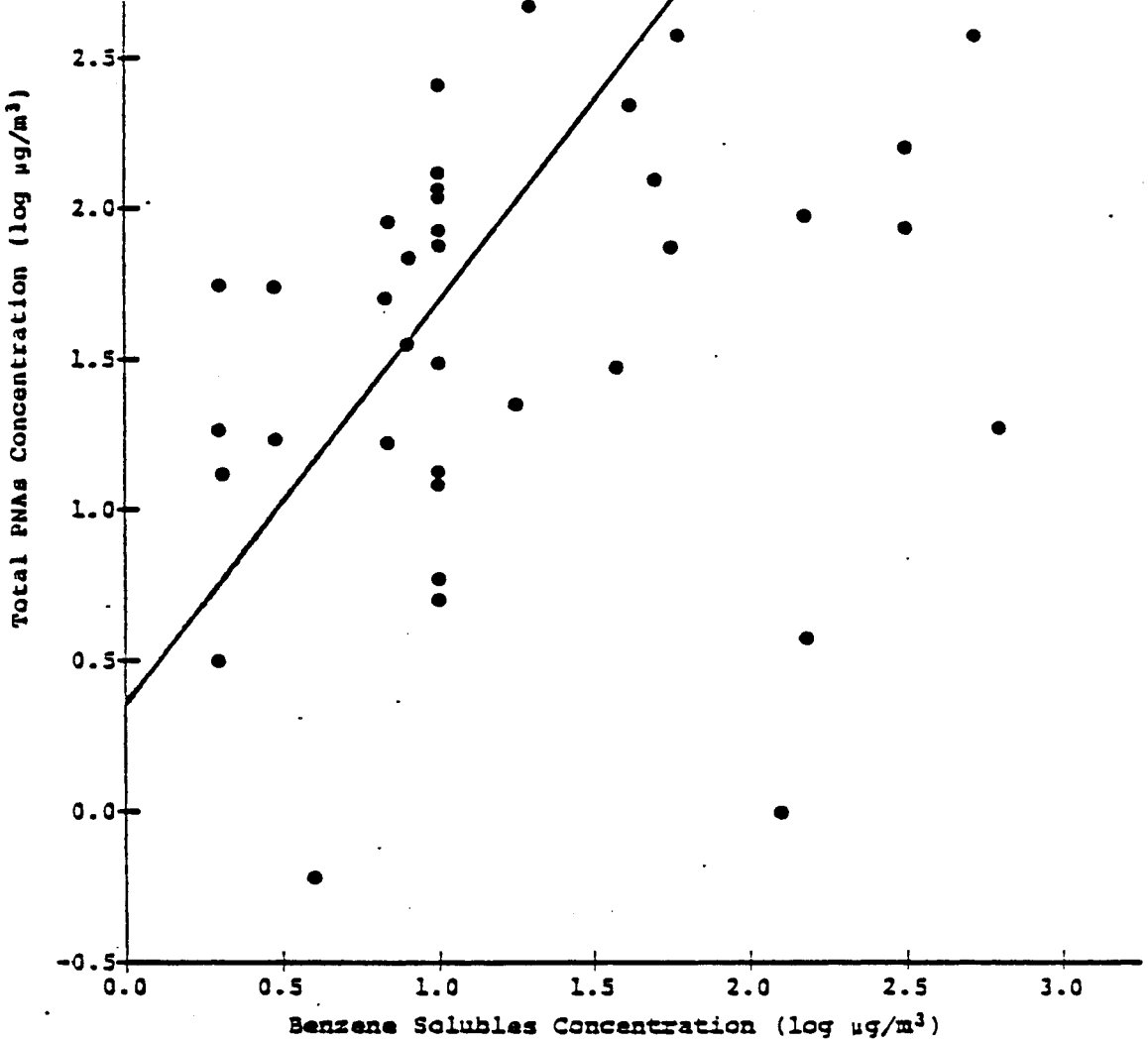

Figure 5. Scattergram: Concentrations of total PNAs vs. benzene solubles measured at two coal liquefaction plants (r = 0.2367)

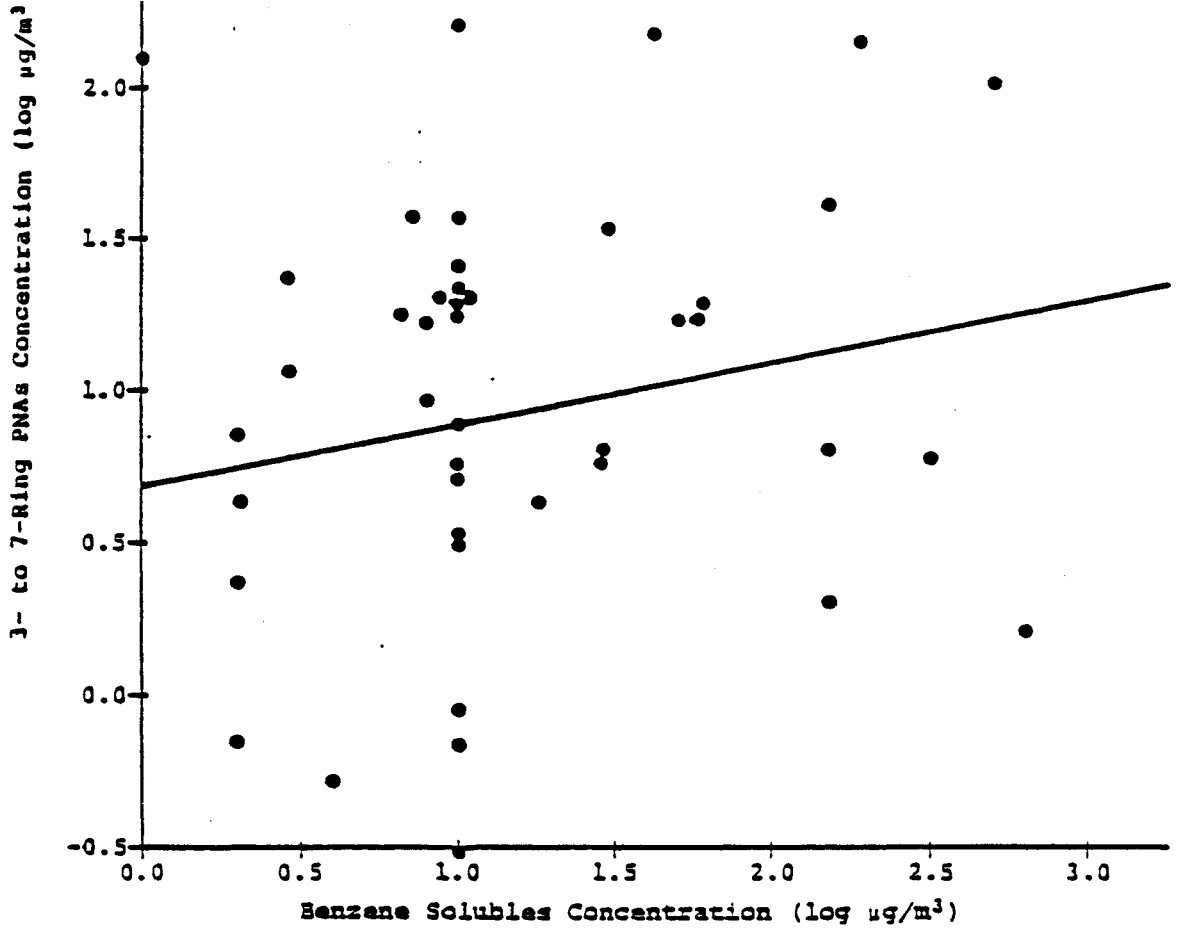

Figure 6. Scattergram: Concentrations of 3- to 7-ring PNAs vs. benzene solubles measured at two coal liquefaction plants (r = 0.1981)

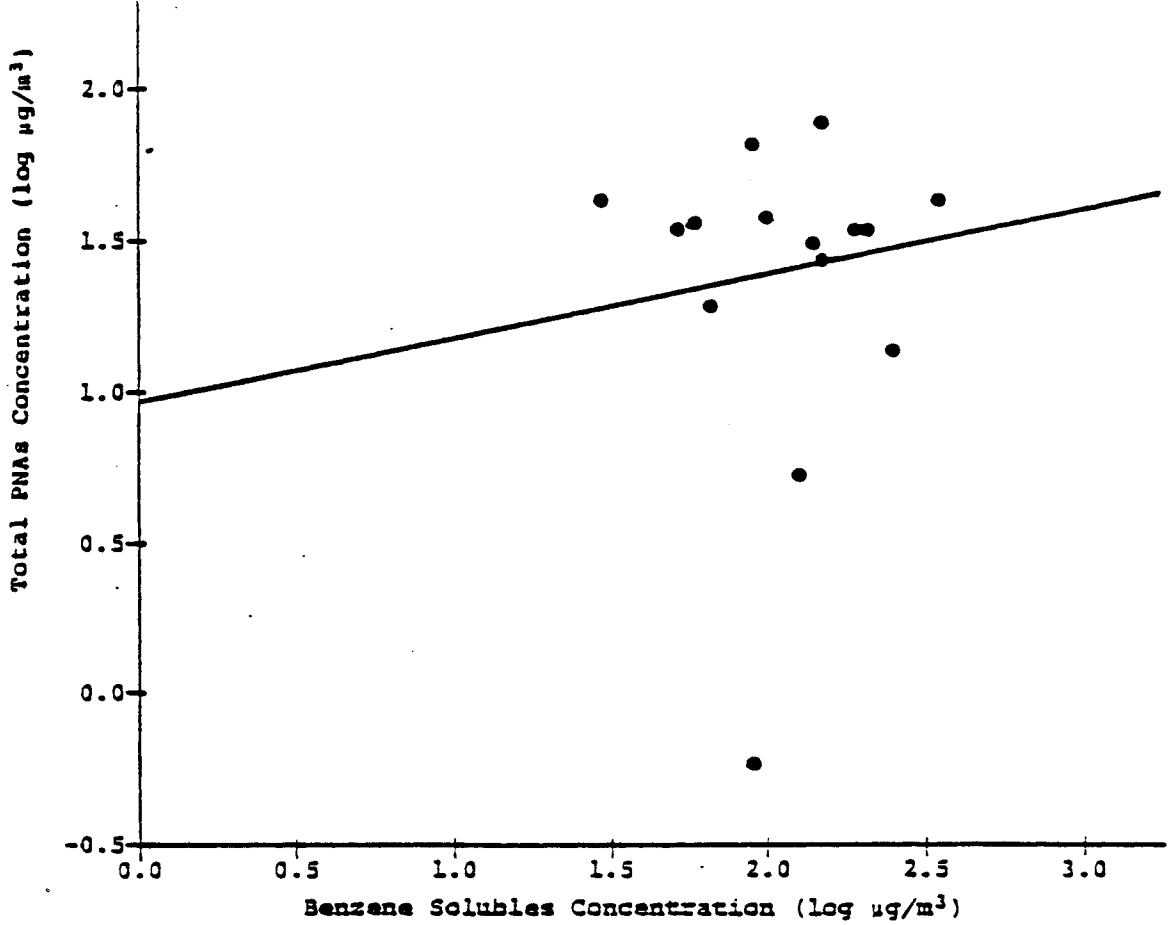

Figure 7. Scattergram: Concentrations of total PNAs vs. benzene solubles measured at a coal gasification plant (r = 0.115)

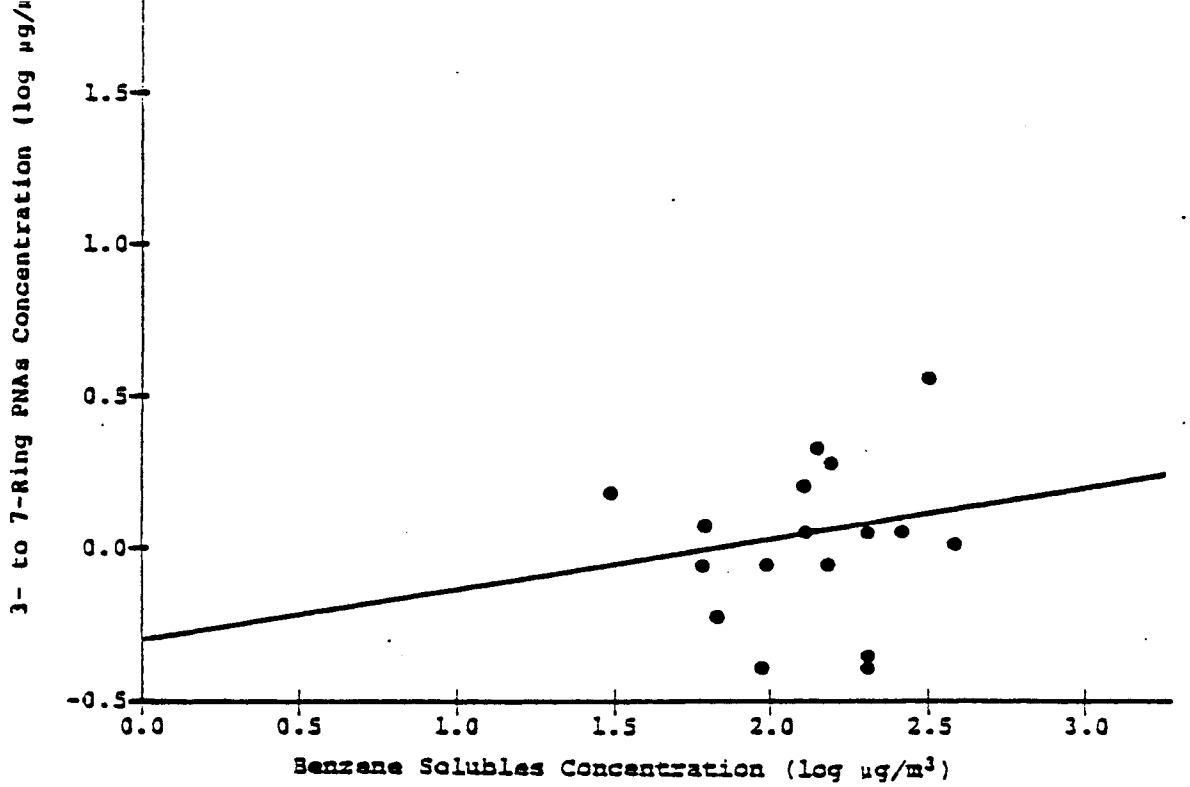

Figure 8. Scattergram: Concentrations of 3- to 7-ring PNAs vs. benzene solubles measured at a coal gasification plant (r = 0.188)

traditional method of measuring the 'benzene-soluble fraction' as an indication of PNA exposure levels. However, variability in desorption efficiencies of this material requires further study.

Analytical procedures requiring GC/MS introduce substantial variability in results. Methods such as capillary column GC or HPLC can reduce instrument variability if the PNAs of interest are not masked by interfering compounds.

Chromosorb 102 has retention characteristics that retain trapped PNAs for full 8-hour shift sampling. Sample loss was not found to be a problem with the concentration ranges found in the three industrial hygiene studies in coal gasification and liquefaction plants and petroleum refineries. Stability of trapped PNAs was not significantly affected by storage up to 30 days.

Comparison of results obtained on the cyclohexane-soluble fractions and actual total PNAs on individual samples showed no direct relationship. Although the PNAs quantitated in the study do not comprise the entire spectrum of substituted and nonsubstituted species present, there was a sufficiently large number quantitated for meaningful comparison with the cyclohexane-soluble data. Results indicate that, in the case of coal gasification and liquefaction plant environments, the cyclohexane-soluble fraction does not show any direct relationship to total PNA exposure.

It can be concluded from the precision data that a more appropriate method for assessing PNA exposure would be the selection of representative PNAs for sampling with analysis by conventional GC or HPLC methods.

and analytical restrictions as well as toxicity.

3. Standard analytical methods, not requiring the GC/MS, should be developed. The methods should be specific for PNAs of up to 5 rings.

4. Use of cyclohexane- or benzene-soluble fractions as an indicator of PNA exposures should be discontinued.

Liquefaction Plants. Final Summary Report prepared for NIOSH under Contract No. 210-78-0101. Dynamac Corporation, Rockville, Maryland.

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