

REPORT ON ANALYTICAL METHODS
USED IN A COKE OVEN EFFLUENT STUDY

THE FIVE OVEN STUDY

K.A. Schulte
D.J. Larsen
R.W. Hornung[†]
J.V. Crable

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Laboratories and Criteria Development
Cincinnati, Ohio 45202
May 1974

HEW Publication No. (NIOSH) 74-105

Single copies are available from:
Office of Technical Publications
National Institute for Occupational
Safety and Health
Post Office Building
Cincinnati, Ohio 45202
(513/684-2723)

Please include a self-addressed mailing label to assist in answering your request.

BIBLIOGRAPHIC DATA SHEET	1. Report No. NIOSH-74-105	2.	3. Recipient's Accession No.
	4. Title and Subtitle Report on Analytical Methods Used in a Coke Oven Effluent Study		5. Report Date May 1974
7. Author(s) K. A. Schulte, D. J. Larsen, R. W. Hornung, J. V. Crable		6.	
9. Performing Organization Name and Address National Institute for Occupational Safety and Health 4676 Columbia Pkwy. Cincinnati, Ohio 45226		8. Performing Organization Rept. No.	
		10. Project/Task/Work Unit No.	
		11. Contract/Grant No.	
12. Sponsoring Organization Name and Address Same		13. Type of Report & Period Covered	
		14.	
15. Supplementary Notes			
16. Abstracts A coking oven study was conducted to evaluate sampling procedures and analytical methods for use in a coke oven effluent study. Selected chemical analysis of airborne particulates, vapors, and metals in the emission from five coke ovens were made. Eight sampling procedures and seven analytical techniques were examined in the study. Correlation coefficients on five of the analytical methods are given.			
17. Key Words and Document Analysis. 17a. Descriptors Coking Sampling			
17b. Identifiers/Open-Ended Terms Analytical methods Sampling procedures Coke oven effluent study Correlation coefficients			
17c. COSATI Field/Group 6J			
18. Availability Statement Release Unlimited		19. Security Class (This Report) UNCLASSIFIED	
		20. Security Class (This Page) UNCLASSIFIED	
		22. Price PC A13-A01	

TABLE OF CONTENTS

INTRODUCTION

EXPERIMENTAL

RESULTS

DISCUSSION

ACKNOWLEDGEMENTS

REFERENCES

APPENDIX A

Method 1.	PSM-1013	Soxhlet Extraction of Benzene Soluble Material in Airborne Particulates Trapped on Silver and/or Glass Fiber Filters.
Method 1.	PSM-1013a	Sampling and Soxhlet Extraction of Benzene Soluble Material in Airborne Particulates Trapped on Hi-Vol Filters (Glass Fiber).
Method 2.	PSM-1016	Gas Chromatographic and Ultraviolet Spectrophotometric Determination of Polynuclear Aromatic Compounds in Airborne Particulates.
Method 3.	PSM-1017	Fluorometric Determination of Benzo(a)Pyrene in Airborne Particulates after Thin Layer Chromatographic Separation.
Method 4.	PSM-1019	Liquid Chromatographic Separation and Spectrophotometric Determination of Polynuclear Aromatic Hydrocarbons in Airborne Particulates after Soxhlet Extraction.
Method 5.	PSM-1014	Composite Emission Index of Volatile Matter Collected on Air Sampling Filters.
Method 5.	PSM-1014a	Composite Emission Index of Volatile Matter Collected on Hi-Vol (Glass Fiber) Filters.
Method 6.	PSM-1020	Determination of Trace Metals in Airborne Particulates by Atomic Absorption Spectrophotometric Techniques.
Method 7.	PSM-1015	Gas Chromatographic Determination of Benzene, Toluene, Xylene, and Napthalene Adsorbed in Charcoal.
Standards	PSM-1018	Purification and Separation by Liquid Chromatography to Produce Ultrapure Compounds.

APPENDIX B

<u>Table</u>	<u>Title</u>
I	Fixed Samplers, Round I, Benzene Soluble
II	Fixed Samplers, Round II, Benzene Soluble
III	Fixed Samplers, Round I, BaP
IV	Fixed Samplers, Round II, BaP
V	Fixed Samplers, Round I, L.C. for 9 PNA's
VI	Fixed Samplers, Round II, L.C. for 9 PNA's
VII	Fixed Samplers, Round I, GC-UV for 14 PNA's
VIII	Fixed Samplers, Round II, GC-UV for 14 PNA's
IX	High-Volume, Round I, B.S., BaP, L.C.
X	High-Volume, Round II, B.S., BaP, L.C.
XI	High-Volume, Round I, AA for 6 Metals
XII	High-Volume, Round II, AA for 6 Metals
XIII	High-Volume, Round I, GC-UV for 14 PNA's
XIV	High-Volume, Round II, GC-UV for 14 PNA's
XV	Personals, Round I, B.X., BaP
XVI	Personals, Round II, B.S., BaP
XVII	Personals, Round I, GC-UV for 14 PNA's
XVIII	Personals, Round II, GC-UV for 14 PNA's
XIX	Charcoal Tubes, Round I, GC for 4 Solvents
XX	Charcoal Tubes, Round II, GC for 4 Solvents

APPENDIX C

1. Memorandum dated October 30, 1972; from Experimental Statistics Section, DLCD to Physical and Chemical Analysis Branch; subject: "Correlations between certain pair-wise combinations of four chemical analytical methods used on four sampling methods for the Coal Tar Pitch Study."
2. Memorandum dated February 14, 1973; from Statistical Services Section, DLCD to Physical and Chemical Analysis Branch; subject: "Determination of sampling and analytical errors in data from Coal Tar Pitch Volatiles Study."
3. Memorandum dated March 29, 1973; from Statistical Services Section, DLCD to Physical and Chemical Analysis Branch; subject: "Correlations between trace metal concentrations and coal tar pitch volatile concentrations determined by several chemical analytical methods."
4. Memorandum dated April 12, 1973; from Statistical Services Section, DLCD to Physical and Chemical Analysis Branch; subject: "Report on statistical analysis of coal-tar pitch volatile data from Union Carbide contract."

TABLES AND FIGURES

- Table I - Sampling and Analytical Schema
- Figure 1 - Benzene Soluble Fraction (mg/m³) of Hi-Vols (RD. I)
- Figure 2 - Benzene Soluble Fraction (mg/m³) of Hi-Vols (RD. II)
- Figure 3 - Benzene Soluble Fraction (mg/m³) of Personals (RD. I)
- Figure 4 - Benzene Soluble Fraction (mg/m³) of Personals (RD. II)
- Figure 5 - Benzene Soluble Fraction (mg/m³) of Personals (RD I vs. RD II)
- Table II - Correlation Coefficients: Benzene Soluble vs. GC-UV and TLC Data
- Figure 6 - RD. I : BaP by Three Methods
- Figure 7 - RD.II : BaP by Three Methods
- Table III - Comparison of Methods of Analysis for Benzo[a]Pyrene
- Table IV - Mean Concentration of 14 PNA's
- Table V - Comparison of the Total Concentration of 14 PNA's with the Total Concentration of the Carcinogenic subset
- Table VI - Comparison of Trace Metal Concentration and Concentration of Organic Material

REPORT ON ANALYTICAL METHODS
USED IN A COKE OVEN EFFLUENT STUDY

ABSTRACT

A coking oven study was conducted by NIOSH to evaluate sampling procedures and analytical methods. Selected chemical analysis of airborne particulates, vapors, and metals in the emission from five coke ovens were made. Eight sampling procedures and seven analytical techniques were examined in this study. Correlation coefficients on five of these analytical methods are given.

I. Introduction

Exposure to coal tar pitch volatiles poses a serious occupational health problem. The problems connected with coal tar pitch volatiles exposure, discussed in detail by W.C. Hueper,¹ are found in such diversified areas as operations connected with tar production, coke ovens, petroleum distillers, and shale and lignite distillation plants. In addition, workers involved in the fractionation of tar and the production of pitch and asphalt, the production of aluminum, the manufacture of building materials and roofing paper, and the construction and maintenance of roads face similar exposure problems. Other industries, such as the electrotechnical, shipbuilding, and fishing trades use tar, pitch, or asphalt in the manufacture of diverse products.

As mentioned above, workers on coke oven batteries are exposed daily to coal tar pitch volatiles. Coke is produced by baking coal in ovens at temperatures near 2800°F for 15 to 20 hours. During this baking process, volatile matter is emitted from the ovens. Most of the emissions are collected by an exhaust ventilation manifold, but a considerable amount of the volatiles do leak into the atmosphere during oven charging (filling) and pushing (emptying) and through faulty door and charging port seals.

A statistical investigation of the mortality of coke oven workers was conducted by Lloyd.² He found that coke oven employees have from 2.5 to 5 times greater incidence of lung cancer than the general population. Exposure to coal tar pitch volatiles is thought to cause this increase. The Pennsylvania Department of Health has conducted a limited study on

coking facilities and found that the average exposure to coal tar pitch volatiles, as indicated by 319 personal samples, was 2.08 mg/m³ benzene soluble material.³ Concentrations ranged from "none detected" to 17.87 mg/m³. The Occupational Safety and Health Standard for exposure to coke oven emissions is 0.2 mg/m³ of benzene soluble material in the air.⁴ The Pennsylvania study found that 92.2% of all samples collected were greater than the maximum allowable concentration.

Coal tar pitch volatiles contain, among many other compounds, polynuclear aromatic hydrocarbons (PNA's). Approximately 10% of the coal tar is PNA's and at least 100 of the compounds in coal tar pitch are either well established or suspected carcinogens. One of these, benzo[a]pyrene (BaP), has been strongly linked with cancer in animal studies. BaP constitutes about 1% of coal tar. The link between BaP and lung cancer in humans is still uncertain. There has been general acceptance (without proof) that the presence of BaP in cigarettes can cause cancer. However, Dr. E.C. Hammond of the American Cancer Society recently reported that 6,000 roofers, who were exposed to large doses of coal tar pitch volatiles daily, showed no greater incidence of lung cancer than the average man.⁵ Dr. Hammond pointed out that roofers inhale amounts of BaP in an average work day equivalent to 35 packs of cigarettes.

The question of the significance of BaP or other PNA's in coal tar pitch volatiles looms large and the possibility of other agents such as trace metals, asbestos, etc. having some role in the production of lung cancer in coke oven workers seems to have relevancy. One theory of

carcinogenesis is that particulates or PNA's alone do not produce sufficient biological response to begin the cancer development, but that when the PNA's are adsorbed onto particulates, in combination with trace quantities of metals, the biological response is sufficient to trigger the cancer mechanism.

At present, sufficient information is not available to determine which constituents of coal tar pitch volatiles present the most danger. Epidemiological studies must be undertaken to determine this. In conjunction with these studies, it is necessary to evaluate various sampling and analytical methods for coke oven emissions so that a chemical characterization of the respirable fraction of the volatiles and particulates can be made.

The National Institute for Occupational Safety and Health (NIOSH) has begun this evaluation by conducting a study, in conjunction with the American Iron and Steel Institute (AISI) to evaluate sampling procedures and analytical methods for coal tar pitch volatiles. This study concentrated on the coal tar pitch volatiles exposure from coke oven emissions. NIOSH held the responsibility for designing and procuring the sampling equipment used in the study and for collecting and analyzing the samples. The AISI supplied technical information from their experience with sampling of this nature and recruited five steel plants, representing the major coal mining areas of the United States, for participation in the program. This study, in addition to providing information on sampling and analytical techniques, will also aid NIOSH in evaluating the current Occupational Safety and Health Standard for coal tar pitch volatiles exposure.

II. Experimental

The sampling program was divided into two parts, which were designated Round I and Round II. Each round consisted of one week of sampling at each of the five plants. Round I was completed in June 1971 and Round II in January 1972. Altogether, 1,440 samples were collected by eight different sampling methods and analyzed by seven analytical methods.

Two types of samplers were used: area samplers, operated at a given station in the plant; and personal samplers, worn by the coke oven employees.

The area samplers consisted of a package of seven different samplers.

These were:

1. A Dorr-Oliver* 10-mm cyclone operated at 1.7 liters per minute, exhausting into a filter held by a 37-mm Millipore Field Monitor Cassette - chosen for a respirable sample with a widely used device.
2. A British Cast Iron Research Association (BCIRA) aluminum alloy cyclone operating at 2.0 liters per minute, exhausting into a filter held by a 37-mm Millipore Field Monitor Cassette - chosen for a respirable sample to compare with the Dorr-Oliver cyclone.
3. A five plate horizontal elutriator operating at 5.0 liters per minute, exhausting into a filter held by a 37-mm Millipore Field Monitor Cassette, chosen because it is a fairly well established method for sampling respirable particulates.
4. A filter held in a 37-mm Millipore Field Monitor Cassette operated with the face cap removed at 5.0 liters per minute, with inlet facing down - chosen to collect a gross sample at a flow rate near the rate for peak efficiency of a filter.

5. Same as (4), but with a different filter type for comparison.
6. A charcoal tube sampled at 0.5 liters per minute to sample for organic solvents.
7. A General Metal Works high-volume air sampler with an 8" x 10" glass fiber filter type without an organic binder, operated at 20 cubic feet per minute - chosen in order to get a sample large enough for analysis by all the chemical methods used.

The first six of the above samplers were attached to a small carrier. The carrier samplers (1-6) and the high-volume unit (7) were operated in close proximity to collect a simultaneous sample in approximately the same area of contamination.

The second type of sampler, the personal sampler, was used to collect samples in the breathing zone of the workers. A personal unit consisted of a Mine Safety Appliance, Model G, battery operated vacuum pump with pulsation dampener operated at 1.7 liters per minute with a Dorr-Oliver 10-mm nylon cyclone which exhausted into a filter held by a 37-mm Millipore Field Monitor Cassette.

The initial selection of filter type for samplers 1-4 was 37-mm silver membrane filters, 0.8 μ pore size, backed up with 37-mm perforated stainless steel pads. Sampler No. 5 was to use a 37-mm glass fiber filter without organic binders, also backed up with the stainless steel disc. However, during the preliminary sampling at a coke battery, it was discovered that many of the filters would load up rapidly with a resulting decrease in flow. In an effort to eliminate this problem, many combinations of filters and back-ups were tried. The optimum combination was found to be a glass

fiber filter without organic binders, followed with a silver filter and backed up with a cellulose pad. This combination was then used in samplers 1-4 and in the personal samplers. A single glass fiber filter without organic binders, with a cellulose backup pad was used for sampler 5.

The seven analytical methods which were used are found in Appendix A. A brief description of each follows:

Method 1. Benzene soluble extract, Appendix A, PSM 1013 and 1013a.

This method involves an extraction of the filter with hot benzene using a Soxhlet extractor and a determination of the weight of the benzene soluble material by the difference between the filter weights before and after extraction.

Method 2. Gas chromatography for polynuclear aromatic hydrocarbons, Appendix A, PSM-1016

This method requires the gas chromatographic separation of fluoranthene, pyrene, benz(c)acridene, chrysene, benz(a)anthracene, benz(a)anthrone, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, dibenz(a,h)-anthracene, benzo(g,h,i)perylene, and anthanthrene using a 3% Dexsil 300 GC column. Identification and quantitation were done using either a UV-Vis spectrophotometer or a spectrophotofluorometer. The sample was transferred from the GC to the spectrophotometer by means of a trapping assembly.

Method 3. Thin layer chromatography for benzo(a)pyrene, Appendix A, PSM-1017

BaP is separated from other aromatic hydrocarbons using thin-layer chromatography. The developing solvent is a pentane-ether mixture.

The BaP is extracted from the plate with diethyl ether and ultimately dissolved in H_2SO_4 . BaP content is measured fluorometrically at 470 nm excitation and 540 nm emission wavelengths.

Method 4. Liquid column chromatography for polynuclear aromatic compounds, Appendix A, PSM-1019

Pyrene, fluoranthene, benz(a)anthracene, chrysene, benzo(e)pyrene, benzo(a)pyrene, perylene, benzo(k)fluoranthene, and anthanthrene were separated using an alumina-packed column and n-pentane-ether mixtures as elution solvents. The fractions collected are scanned by absorption spectroscopy and specific fractions are examined by fluorometry in order to quantitate the amounts present.

Method 5. Emission Index, Appendix A, PSM-1014 and 1014a.

The sampling filters are extracted with cyclohexane partitioned with a dimethylsulfoxide-phosphoric acid mixture, and then partitioned with iso-octane. The iso-octane extract is used to obtain the UV-Vis spectrum from 200-600 nm, the fluorometric emission spectra from 300-500 nm with excitation at 350, 400, and 450 nm, and the fluorometric excitation spectra from 300-500 nm with emission at 350, 400, and 450 nm.

Method 6. Trace metals by atomic absorption, Appendix A, PSM-1020

The filter samples are wet-ashed with ultra-pure acids and the resulting ash is taken into solution and diluted to 25 ml. The solution is analyzed using the atomic absorption spectrophotometer for cobalt, chromium, copper, manganese, nickel, and zinc.

Method 7. Gas chromatography for organic solvents, Appendix A, PSM-1015

Organic solvents in the atmosphere are collected on activated charcoal and then desorbed from the charcoal by carbon disulfide.

An aliquot of the CS₂-solvent solution is injected into a gas chromatograph and the recorded areas under the benzene, toluene, xylene, and naphthalene peaks are integrated. An 8% SE-30 column was used to attain separation.

The division of the samples among the sampling and analytical techniques is shown in Table I. This report will deal only with the evaluation of analytical methods.

III. Results

The initial effort in this study consisted of setting up the seven analytical methods for routine sample analysis. During this period, several modifications of the literature methods were made in order to facilitate routine analyses. These modifications are incorporated in the Parma Standard Methods (PSM) enclosed in Appendix A. Additional PSM's were written for two of the methods to document changes necessary for handling the high volume filters. One other PSM describes purification of the polynuclear aromatic hydrocarbons used as standards.

The use of these analytical methods routinely gave us an insight into the strength and weaknesses of the methods. The information we acquired from repeated usage of the methods follows:

Method No. 1 - Benzene solubles⁶

The determination of the quantity of benzene soluble material in airborne particulates, collected on different filter materials

in various combinations, was set up following the general method outlined by Richards, et al.⁷ Approximately 800 samples were analyzed by this method including several sampling blanks.

This method is easy to follow, requires little sophisticated or expensive equipment, and can be operated by relatively inexperienced technicians with a minimum of supervision. However, several aspects of this analysis could lead to error and should not be overlooked:

(1) humidity variations can cause considerable variations in weights; (2) some of the particulates do not adhere well to the silver membrane filters; (3) particulates are frequently washed off the filters during extraction and are quite hard to quantitatively recover; (4) the filters themselves sometimes fray during handling and extraction, and these small pieces can be inadvertently lost; and (5) the filters will not hold their weight to less than 0.1 mg, thereby limiting the results to ± 0.1 mg/filter. The incorporation of a glass fiber filter appears to lower the problem of particulate loss.

The determination of the benzene soluble materials trapped on the high-volume filters incorporates the use of a glass crucible to hold the sample. This procedure eliminates loss of particulates, but increases the care that must be taken to maintain equivalent humidity for both weighings. When these samples are heavily loaded with benzene soluble particulates, the extraction time must be extended for complete solution of the soluble materials. In the case of heavy loading, one-eighth or less of the filter is adequate for extraction.

We considered our detection limit to be 0.1 mg of benzene soluble material. The weight of all filters which exhibited no weight change,

or whose weight change was less than 0.1 mg was reported as <0.1 mg in the data tables of Appendix B.

Method No. 2 - Gas Chromatography for Polynuclear Aromatic Compounds⁸

The method for the gas chromatographic (GC) analysis of 14 polynuclear aromatic compounds (PNA's) was adapted from the method by Searl, et al.⁹ and was used for over 500 samples. Several changes were made in the literature method in order to include all 14 PNA's and in order to better quantify the results from the samples which included many additional compounds. The major changes were:

(1) use of Dexsil 300-GC liquid phase for high temperature stability and longer column life; (2) use of two internal standards (o-terphenyl and bibenzyl) with integrator area for both compounds and UV area for o-terphenyl available for calculation purposes; and (3) use of stainless steel injection liner at 350°C injection temperature.

Mass spectrometer analysis was used as a support for verification of the UV identification of the 14 PNA's. The following briefly summarizes the mass spectrometric data: (1) verification of the purity of the synthesized benzo(j)fluoranthene-mol. wt. 252; (2) identification of the mol. wt. of 178 for the impurity eluting with the o-terphenyl internal standard (GC retention time data and UV spectral data verify phenanthrene); (3) identification of the mol. wt. of two components (230 and 246) not included in the analysis but which constitute the major peak in many samples; and (4) suggestion of the presence of an isomer of dibenz(a,h)anthracene in the fraction for that compound. In addition, the mass spectrometric analysis of the benz(c)acridine fraction did not verify the presence of

benz(c)acridine in sample traps, even though spectral analysis indicated it to be present. Mass spectrometric analysis of the trapping of the benz(c)acridine standard was positive. It appears that some interfering compounds elute with benz(c)acridine and also have an absorption peak at 384 nm. From these facts, the analysis of benz(c)acridine is unsatisfactory. Mass spectral data would be necessary of each sample for verification. The method as outlined in PSM-1016 is satisfactory for the analysis of a large number of PNA's.

There are several factors which should be considered for improvements in the analysis: (1) determination of a better internal standard, because the large number of components in the "heavy" samples frequently interfere with the internal standard, (2) elimination of benz(a)anthrone, which was never found in over 500 samples; (3) further study of the dibenz(a,h)anthracene fraction for isomers; (4) further study of the benz(c)acridine fraction in order to find a satisfactory method for analysis of this compound; and (5) consideration of modifying the analysis so that fewer compounds are analyzed.

The detection limits for this method, based on the entire filter being analyzed, were:

Fluoranthene	0.4 µg
Pyrene	0.3 µg
Benz(c)acridine	1.4 µg
Chrysene	0.1 µg
Benz(a)anthracene	0.2 µg
Benz(a)anthrone	1.6 µg
Benzo(b)fluoranthene	0.8 µg
Benzo(k)fluoranthene	0.7 µg
Benzo(j)fluoranthene	0.6 µg
Benzo(e)pyrene	0.5 µg
Benzo(a)pyrene	0.7 µg
Dibenz(a,h)anthracene	0.8 µg
Benzo(g,h,i)perylene	1.6 µg
Anthanthrene	0.3 µg

Method No. 3 - Thin Layer Chromatography for Benzo(a)pyrene¹⁰

This method was readily adapted from that of Sawicki, et al.¹¹ Only slight modifications were necessary to set up a routine analysis of benzo(a)pyrene (BaP). Over 500 samples were run by this method. Several factors have been noted which are potential sources of error. The thin layer chromatography (TLC) separation varies greatly on a day-to-day basis as well as, on occasion, from one side of the plate to the other. The purity of the solvents used for developing the plates, extracting the BaP, and fluorescent measurements causes variations in the absolute value of the fluorescent intensity for standards. The accuracy of this analysis is dependent on these variations affecting equally both standards and samples.

The method improved constantly during the course of the analyses, so that by the end of the study, the detection limit was thought to be 5 ng.

Method No. 4 - Liquid Column Chromatography for Polynuclear Aromatic Hydrocarbons¹²

This method as outlined in the literature,^{13,14} required major modifications before an acceptable routine analytical method was set up. The major changes included: (1) pretreatment of the alumina; (2) quantity of solvents used; (3) elimination of benzo(g,h,i)perylene from the analysis (never separated sufficiently for quantification); (4) analysis of overlapping compounds by use of a computer program to calculate the concentrations from a series of equations; and (5) combination of fractions which contain noninterfering compounds to shorten the time required for analysis.

This analysis, more than any of the other six, is highly operator-dependent. The skill and consistency required are difficult to transfer from lab to lab. We recommend that this method, in its present state, not be considered for adoption as a standard method.

The automated liquid chromatographs appear to offer advantages which could possibly overcome many of the shortcomings of this method. The column is used repeatedly, thereby eliminating variable separations due to column variations. The detectors can be calibrated to quantify the components, thereby eliminating separate analysis for quantification. The possibility of a liquid chromatographic separation and subsequent quantification of PNA's by an automated liquid chromatograph should be investigated. There appears to be a much greater probability of development of a standard method by this means.

No detection limit has been determined on this method. However, we felt that, due to the great amount of manipulation necessary in the method, no value less than 1 μg could be considered valid. Liquid chromatography was performed on only part of the sample. If a sample showed a positive UV response, which after calculations had been performed gave a value less than 1 μg of PNA present, the value was reported as <1 μg ." If there was no response at all to the UV on the aliquot of sample being analyzed, the value was reported as "N.D." All values were reported on the basis of the entire filter, even though only a portion of the filter had been analyzed. Therefore, it is possible that the filters which are reported as "N.D." would have had a detectable amount on them had the entire filter been analyzed.

Method No. 5 - Emission Index¹⁵

During the study over 400 samples were analyzed using this method. It is easily run on a routine basis and, although not quantitative at present, the method could be modified to a semi-quantitative analysis.

Method No. 6 - Trace Metals by Atomic Absorption Spectrophotometric Techniques¹⁶

The atomic absorption spectrophotometric method for determining six trace metals collected on high-volume glass fiber filters was set up using a wet-ashing procedure for the filter, followed by standard atomic absorption spectrophotometric techniques. Since the samples contained high levels of sodium and iron, the interelement effect of both of these metals in the determination of chromium, cobalt, copper, manganese, nickel, and zinc was investigated. There were no significant interferences as a result of the high sodium levels; however, the high iron concentration affected the analyses of manganese, chromium, cobalt, and copper. In some cases the error was of the order of 300%. For satisfactory analyses, the iron concentration must be determined and the interference effects compensated for, either by preparing mixed standards for each sample or by employing the computer program which is included in PSM-1020.

During the process of analyzing the samples, it was observed that the accuracy obtained with this method could be quite dependent upon the wet-ashing procedure. When it is applied to the airborne particulates which have been trapped on high-volume filters, there are a number of inherent drawbacks which include: (1) insufficient leaching

of the trace metals from the relatively large amount of glass fiber filter material present, which itself is not greatly affected by the acids; (2) if the iron content of the sample is high, complete dissolution of the iron is not always accomplished, and as a result, not all of the trace metals will be dissolved; (3) the large number of manipulations and the corresponding length of time involved could introduce or result in the loss of the trace metals being determined; (4) the presence in the airborne particulate material of certain organic compounds which tend to ignite or explode during the evaporation and drying steps, resulting in possible loss of the trace metals as well as a definite safety hazard; and (5) the loss of metals by the formation of insoluble silicates.

There are several areas of this method which should be critically reviewed and investigated before it is considered for adoption as a standard method. Another procedure for dissolving the trace metals might be attempted, such as the total digestion of both the airborne particulates and the high volume filter material with a combination of nitric and perchloric acids. Since the composition of the filter itself is one of the primary concerns in any procedure utilized to take the trace metals into solutions for subsequent analysis, the investigation of alternate filter materials, in order to find one equally suitable in all other respects as the glass fiber or the high volume filter, might be a way of resolving this problem.

After the trace metals are in solution, the use of atomic absorption spectrophotometric techniques to determine the six specified elements is relatively straightforward, providing a

computer program is employed to make the proper corrections for the interference of iron in the chromium, cobalt, copper, and manganese determinations. If a computer program is not used, the number of interference standards which must be prepared to correct for the varying iron interference soon becomes unwieldy, thereby rendering the use of this method almost prohibitive.

The detection limits for the trace metals was considered to be 5 ng.

Method No. 7 - Gas Chromatography for Organic Vapors¹⁷

The method for analysis of solvent vapors was that of White, et al.¹⁸ One modification was made: the liquid phase was changed to SE-30 which is considerably more stable and which greatly improves the naphthalene analyses.

This method requires care in operation since it employs an external standard. However, it has been successfully operated routinely and can be readily set up in other laboratories. When the operator has learned the skill necessary for the analyses, two injections should be sufficient in most cases for satisfactory results.

The detection limit for benzene, toluene, and xylene is 0.1-0.2 μ g. Naphthalene, being a broader peak, has a detection limit of 0.2-0.3 μ g.

After the initial work was completed, routine analysis of the samples began. A total of 2,638 analyses were done. As noted previously, the samples were collected at five different coking operations (denoted as companies A through E in the data tables) and at two different times of

the year for each company. Round I data was obtained from samples collected in the spring of 1971; Round II samples were collected in the winter of 1971. All of the data for the area samplers, except the high volume and charcoal tube data is found in Appendix B, Tables I through VIII. Twelve area samplers were placed at each company during each round. The data in the tables has been arranged so that the analytical results from the samples in the same area carrier are together. That is, all filters which are listed as Co.#A-1 were taken at Company A and located in area sampler number 1. The area carriers in Round I are numbered 1 through 12; those in Round II are numbered 21 through 32. The corresponding high volume and charcoal tube data is found in Appendix B, Tables IX through XIV, XIX, and XX. The numbering in these tables is identical to that of the other tables. Therefore, a charcoal tube numbered Co.#D-2 was located in the same area carrier as a filter numbered Co.#D-2. The Round I and Round II data from the personal samplers are found in Tables XV through XVIII, Appendix B.

After the analytical results had been received and the data had been reduced, the methods were compared and a statistical evaluation of the data begun.

The first comparative studies were done on the results from the benzene soluble analyses. Total benzene soluble concentrations were determined on both high volume and personal samples. Twelve high volume filters were sampled on the catwalks at each of the five batteries during each round of sampling. Figure 1 shows the range, average, and 95% confidence intervals for the average of the benzene soluble data collected from Round I samples. The 95% confidence intervals indicate that a 95% probability exists that the true average concentration for each company

lies within the given interval. The intervals are skewed, not symmetric, about the average because the data are log-normally distributed. Figure 2 illustrates the results of the benzene soluble analysis of Round II samples. In both Round I and Round II, a large portion of the samples lie above the threshold limit value of 0.2 mg/m^3 benzene soluble material. The average benzene soluble concentrations and the 95% confidence intervals of Round II samples were greater than those of Round I.

Figures 3 and 4 illustrate the range, average, and 95% confidence intervals for the personal samples collected during Rounds I and II. As with the high volume samples, most of the personal samples lie above 0.2 mg/m^3 of benzene soluble material.

The average benzene soluble concentration of the personal samples collected at each of the five plants during Rounds I and II is compared in Figure 5. The average benzene soluble concentration for the second round of samples is greater than that of the first at all five companies, for both personal and high volume samples. Several factors may have contributed to this difference: samples collected in Round I were stored for several months in a refrigerator prior to analysis, while the Round II samples were analyzed a few weeks after collection; Round I was sampled in the spring, while Round II was sampled in the winter; operating conditions at the ovens may have changed between sampling rounds.

As stated previously, the Occupational Safety and Health Standard for exposure to coke oven emissions is based on the concentration of benzene soluble material in the air (0.2 mg/m^3 benzene soluble material). This is

a nonspecific standard which does not distinguish between carcinogenic and non-carcinogenic organics. In order to have a more complete characterization of coke oven emissions, we measured the concentration of several polynuclear aromatic hydrocarbons. Three methods were used to determine the PNA content of the coke oven atmosphere: the gas chromatographic-ultraviolet spectrophotometric analysis of 14 PNA's (Method 2), the thin-layer chromatographic method for BaP (Method 3), and the liquid chromatographic analysis for 9 PNA's (Method 4). The results of the benzene soluble analysis were correlated with the PNA content as determined by both the TLC method (BaP only) and the GC-UV method (total of 14 PNA's). The benzene soluble concentration was highly correlated with the BaP concentration as measured by TLC when two of the sampling methods, the high volume sampler and the horizontal elutriator were used. However, with all other sampling devices, the correlation coefficient was quite low. No significant correlation was found between the benzene soluble material and the sum of the concentrations of the 14 PNA's as determined by GC-UV. The correlation coefficients are given in Table II.

The data gathered on benzo(a)pyrene concentration levels were also examined. The BaP levels were measured using three different analytical methods and several sampling techniques. All three of the analytical methods, GC-UV (Method 2), thin-layer chromatography (Method 3), and liquid chromatography (Method 4) were used to determine the BaP levels on each of the high volume filters. Figure 6 is a comparison of the average BaP concentrations of 12 high volume filters from each company as determined by each of the three analytical methods. These data are

taken from Round I samples. The same comparisons were made on Round II data and are expressed in Figure 7. Examination of Figure 6 shows that the BaP concentrations detected by the GC-UV and TLC methods are fairly close, whereas the liquid chromatographic method yielded values twice as high as the other two methods. The analyses of Round II samples resulted in average BaP levels that were in fairly good agreement. Company D, Round II, is a notable exception.

Correlation coefficients for the methods were calculated and are given in Table III. A good correlation exists between the BaP levels found using the thin-layer chromatographic and liquid chromatographic methods, while the correlation is poor between the TLC and GC-UV methods. A high correlation coefficient for two methods indicates that the amount of BaP found by one method is proportional to that found by the other. It does not indicate that the same amount of BaP was detected by both methods.

A gas chromatographic-ultraviolet spectrophotometric analysis for 14 PNA's (Method 2) was performed on four types of samples: high volume filters, personal samples, horizontal elutriators, and gross samples. The average total amount of the 14 PNA's found in each of the sampling types is given in Table IV. Since the high-volume and gross samples monitor the same atmosphere and collect both respirable and non-respirable particulates, the difference in the total amount of PNA's detected using these two sampling devices could reflect a basic difference in the efficiency of the sampling devices and/or the error of the analytical method.

There were definite trends in the detection of the PNA's. In the high-volume, horizontal elutriator, and gross samples, six of the 14 PNA's were most abundant: chrysene, fluoranthene, pyrene, benz(a)anthracene, benzo(k)fluoranthene, and benzo(a)pyrene. Three compounds were present in fairly low concentrations: anthanthrene, benz(c)acridine, and dibenz(a,h)anthracene. The personal samples contained only two major components, chrysene and benz(a)anthracene, and only minute or non-detectable quantities of the other 14. Benz(a)anthrone was not found in any of the high-volume or personal samples, but several compounds besides the 14 were found. One of these additional peaks was identified as phenanthrene and two others were found to have molecular weights of 230 and 246.

A subset of the 14 PNA's was correlated with the entire set in order to develop a less time-consuming method of analysis. The subset consisted of those PNA's which were carcinogenic,¹⁸ benz(a)anthracene, benzo(b)-fluoranthene, benzo(j)fluoranthene, and benzo(a)pyrene, plus the isomers of these compounds which were included in the original 14, benzo(e)pyrene and benzo(k)fluoranthene. The subset, consisting of six compounds, was called the carcinogenic subset.

Correlation coefficients for the total concentration of PNA's in the carcinogenic subset and the 14 PNA total were calculated. These coefficients, given in Table V, were found to be generally greater than 0.9 for all four sampling methods in both Round I and Round II. The high correlation coefficients indicate that the six compounds in the subset will indicate exposure to the total 14 compounds.

The data collected on the high volume filters is fairly consistent. The weight of the benzene soluble extract is generally 20-40% of the weight of the entire sample. The 14 PNA's comprised about 5% of the benzene soluble extract, while the six compounds in the carcinogenic subset consisted of 2%, and the BaP was 1% of the extract.

The trace metal distribution of the high volume filters was investigated and found to be fairly uniform from one sample to another. Over half of the trace metal concentration could be attributed to zinc, while intermediate concentrations of copper and manganese, and only small amounts of chromium and nickel were detected. Correlation coefficients were calculated for the sum of the trace metal concentrations and the benzene soluble concentration, the sum of the 14 PNA's as determined by GC, the BaP concentration determined by TLC, and the sum of the 9 PNA's analyzed by liquid chromatography. These correlation coefficients, presented in Table VI, are low, indicating that there is no correlation between the amount of trace metals present and the benzene soluble or PNA levels.

The charcoal tubes, which were sampled on the catwalks above the ovens, were analyzed for benzene, toluene, xylene, and naphthalene. Although these compounds are cited in the literature as being present in fairly large amounts in coking operations, only microgram quantities were found on the tubes. We suspected that the charcoal tube was not a good collection device at the extreme temperatures and humidities found on a coke oven. However, charcoal tubes which were sampled at a later

date to check the trapping ability of the charcoal contained appreciable quantities of all four organic solvents. Therefore, it is most likely that either benzene, toluene, xylene, and naphthalene were not present in any of the coking operations which were visited, or that some sampling error occurred and these compounds were not trapped.

The emission index spectra which were obtained on some of the samples have not been evaluated as yet, but it is hoped that some characteristics of the spectra can be correlated with the PNA content of the sample.

Discussion

The benzene soluble fraction of coal tar pitch volatiles, upon which the present standard is based, does not correlate well with any of the tested analytical methods for PNA's. This lack of correlation requires that epidemiological studies be conducted to determine if the polynuclear aromatic hydrocarbons will be a good index of the hazards of exposure to coal tar pitch volatiles. It is desirable to find a new analytical method for assessing coal tar pitch exposures because of the obvious drawbacks of the benzene soluble method. As its name implies, the method is non-specific, analyzing for all compounds soluble in benzene. There are also problems involved in the procedure itself: the weights of benzene soluble material may be erroneous due to a disintegration of the filter and loss of particulate during handling and extraction or due to a change in the water content of the filter between the tare and final weight after extraction. We feel that a method which is specific for certain compounds or classes of compounds is needed. At present, no method can be singled out as the best method. More work must be done to determine exactly which components of coke oven emissions are

hazardous and at what concentrations they affect the worker adversely. Once this is known, the Federal standard must be re-evaluated, and suitable analytical methods selected. Gas chromatographic and high-pressure liquid chromatographic methods hold promise, however, because of their specificity and ease of operation.

Acknowledgements

The modification of the published analytical methods and the analyses of all samples were done by Union Carbide Corporation, Cleveland, Ohio, under contract number HSM-099-71-7. We extend special thanks to Dr. Paul Coulter and Mrs. Barbara Petro, both of Union Carbide, for their excellent technical assistance.

We also extend thanks to the personnel of the Hazards Evaluation Services and Engineering Branches, NIOSH, particularly Mr. Jerome Flesch and Mr. Michael Anglin, for their assistance in collecting all of the samples needed for this study.

TABLE I. SAMPLING AND ANALYTICAL SCHEMA

<u>Sampling Procedure</u>	<u>Analyses*</u>	<u>No. of Samples</u>
1. BCIRA cyclone	1 5	60 60
2. Dorr Oliver cyclone	1 5	60 60
3. Gross glass fiber filter	1 5	60 60
4. Gross silver filter	1 & 2 1 & 3 1 & 4 2 & 5 3 & 5 4 & 5	20 20 20 20 20 20
5. Horizontal Elutriator	1 & 2 1 & 3 1 & 4 2 & 5 3 & 5 4 & 5	20 20 20 20 20 20
6. Charcoal tube	7	120
7. Hi Vol glass fiber filter	1,2,3,4,5, & 6	120
8. Personal monitor	1 & 3 2	300 <u>300</u>
		1,440

*Number refers to methods listed previously.

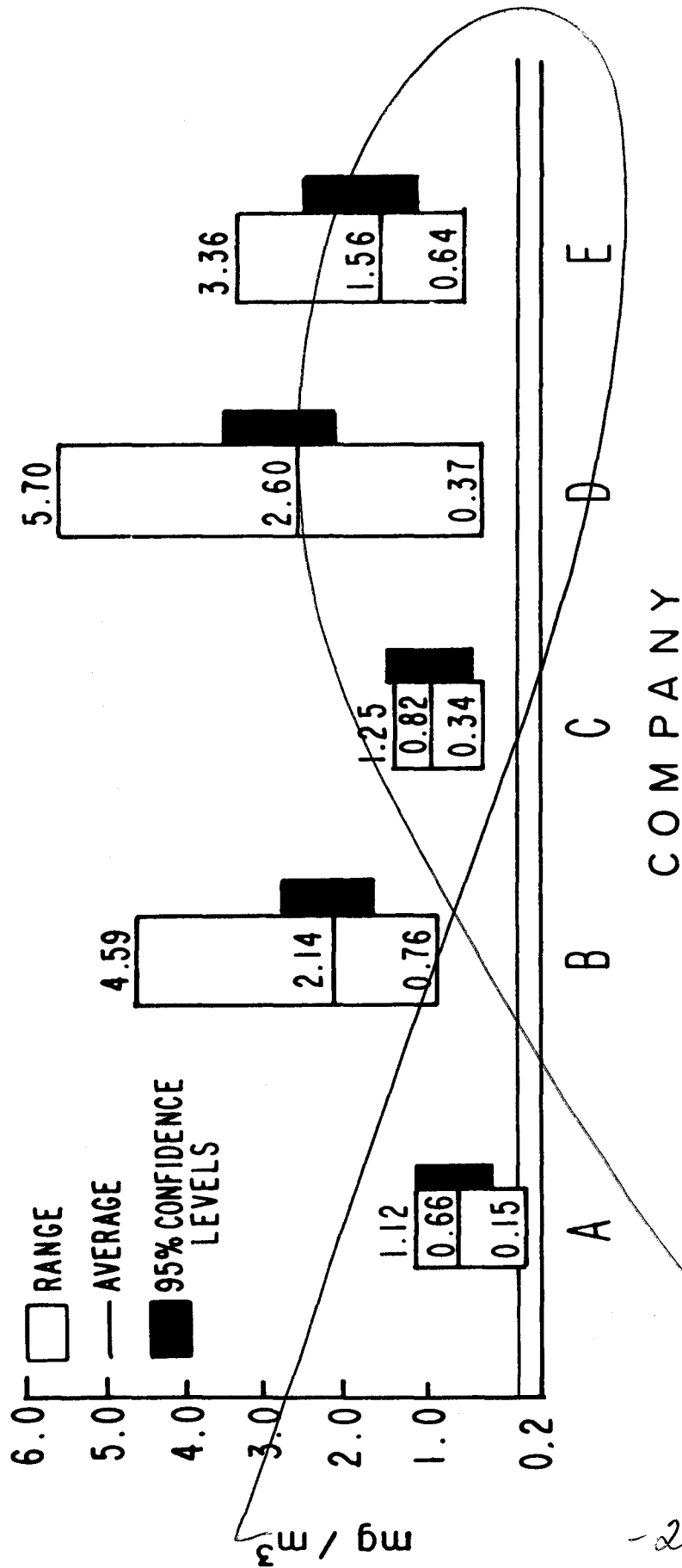


FIGURE 1. BENZENE SOLUBLE FRACTION (mg/m³) OF HI-VOLS (Rd I)

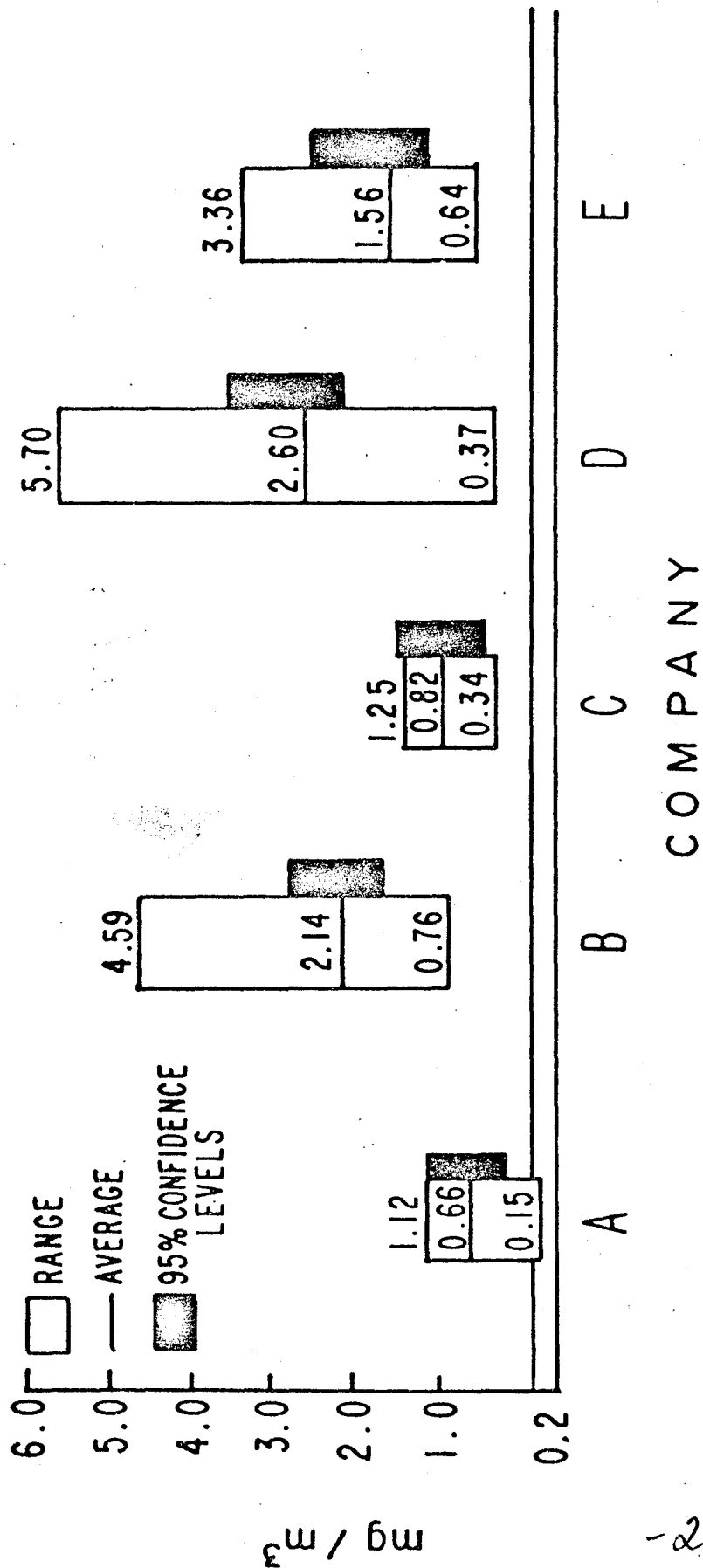


FIGURE 1. BENZENE SOLUBLE FRACTION (mg/m³) OF HI-VOLS (Rd I)

1

1

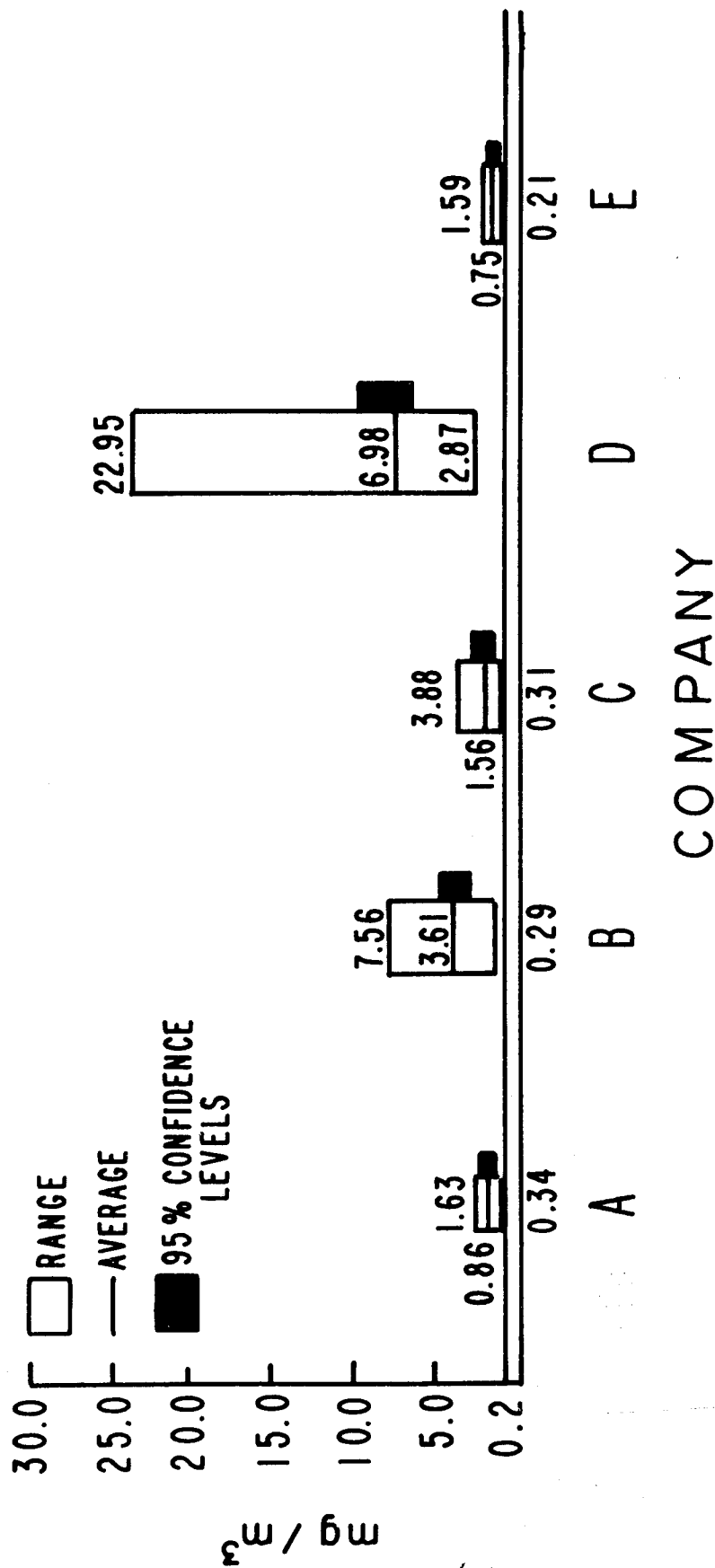


FIGURE 2. BENZENE SOLUBLE FRACTION (mg/m³) OF HI-VOLS (Rd II)

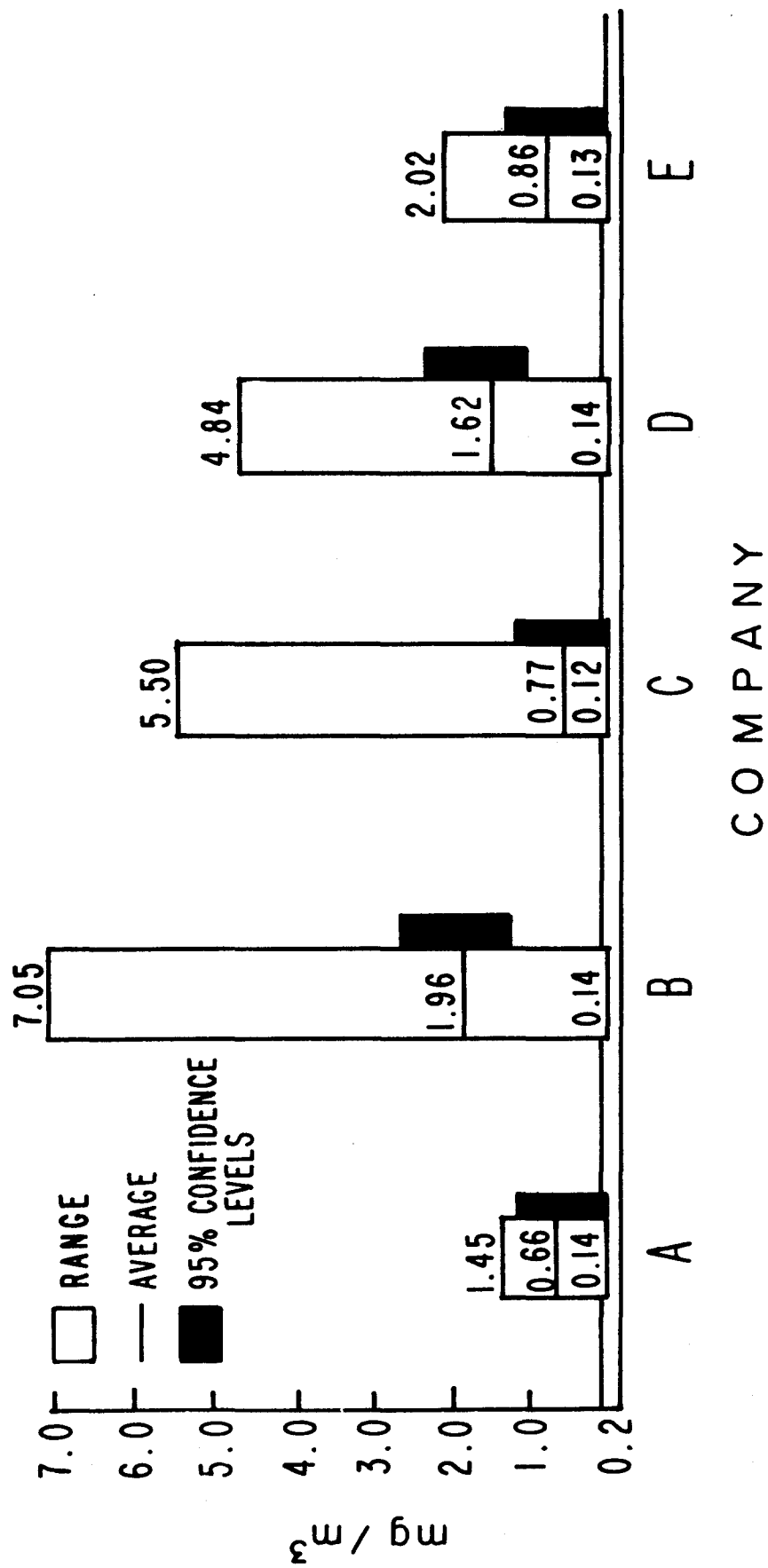


FIGURE 3. BENZENE SOLUBLE FRACTION (mg/m^3) OF PERSONALS (Rd I)

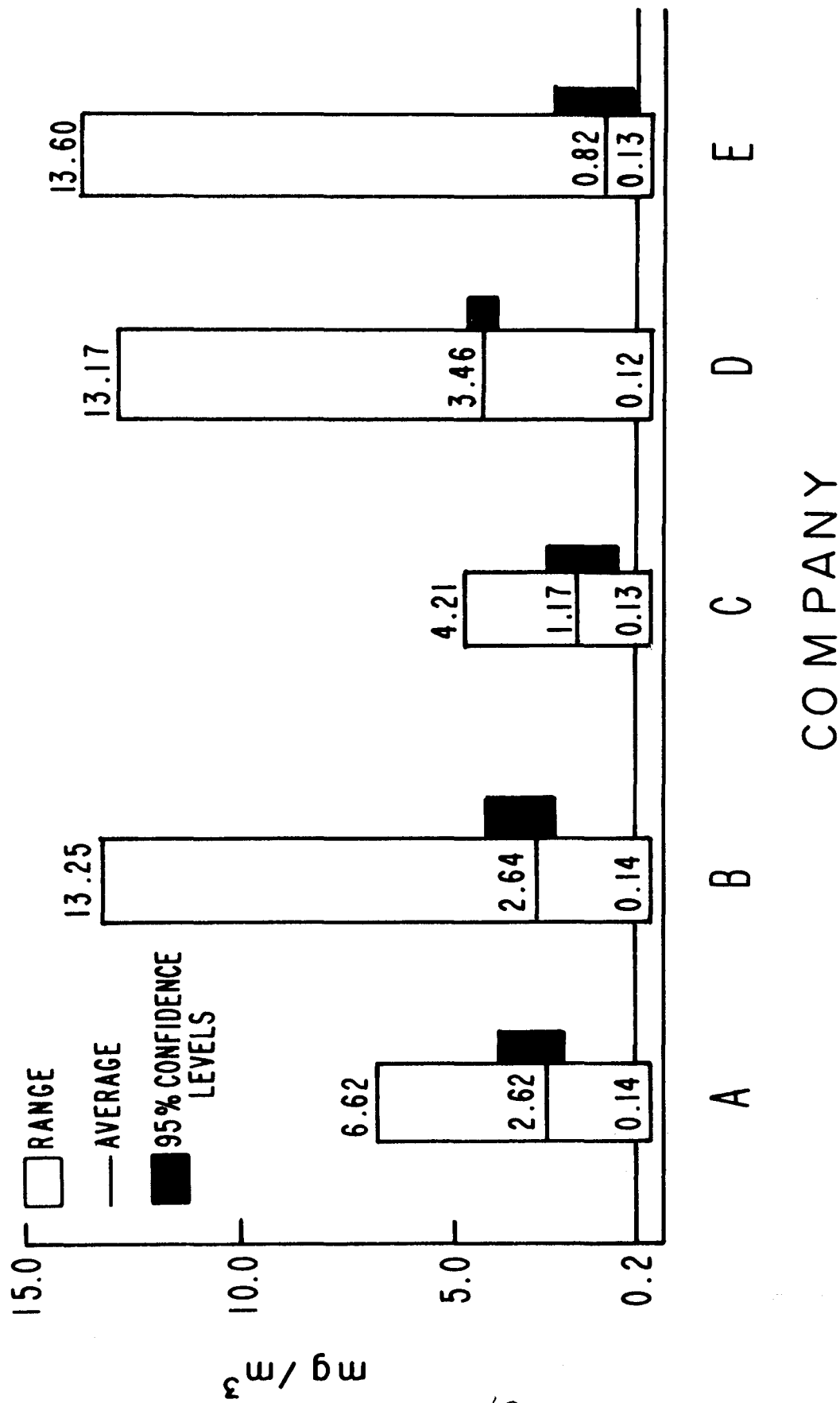


FIGURE 4. BENZENE SOLUBLE FRACTION (mg/m³) OF PERSONALS (Rd II)

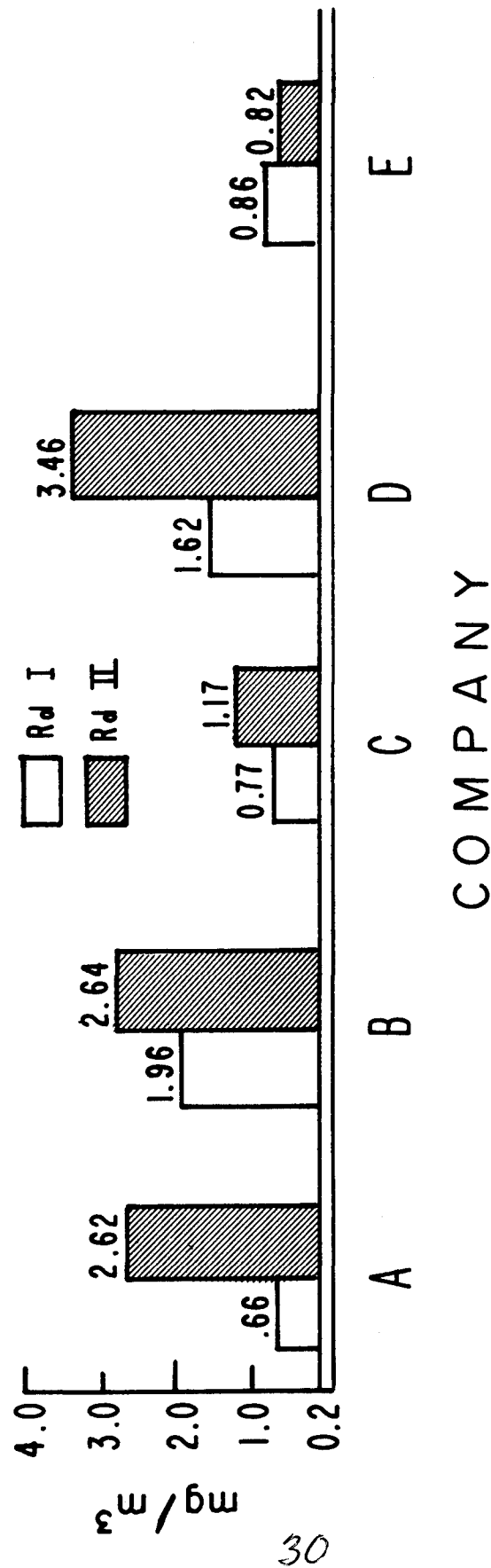


FIGURE 5. BENZENE SOLUBLE FRACTION (mg/m^3) OF PERSONALS (Rd I vs. Rd II)

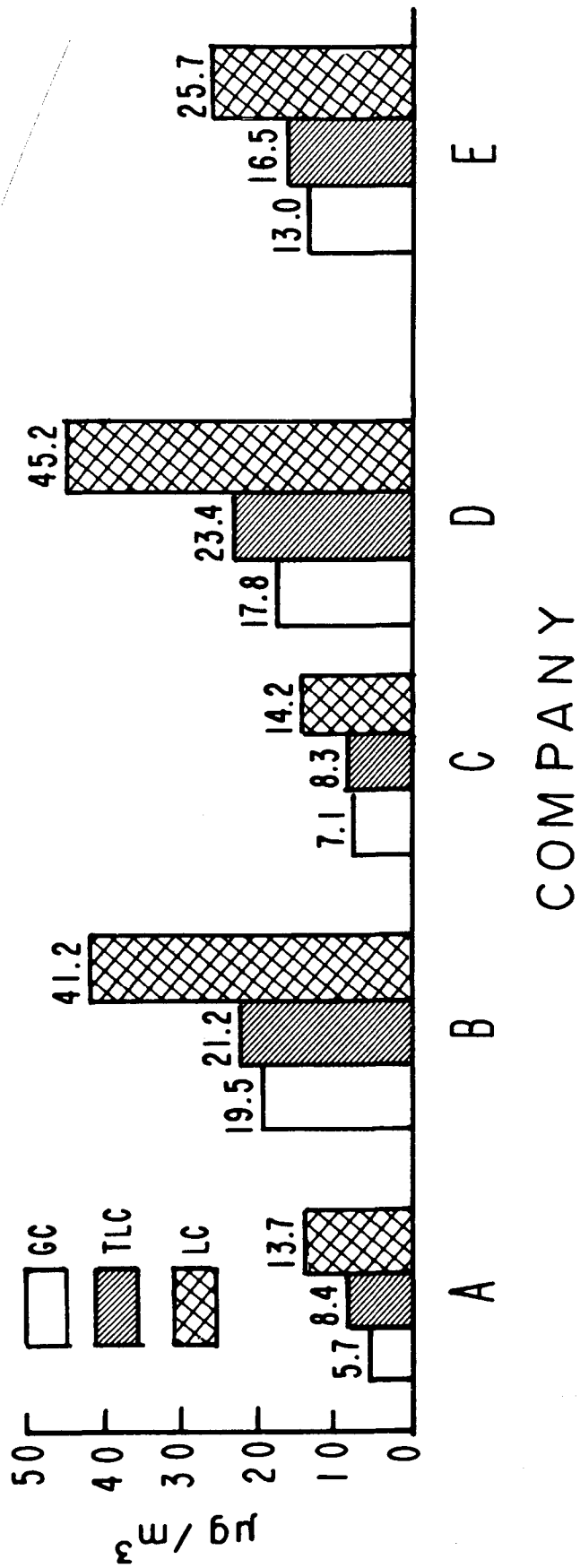
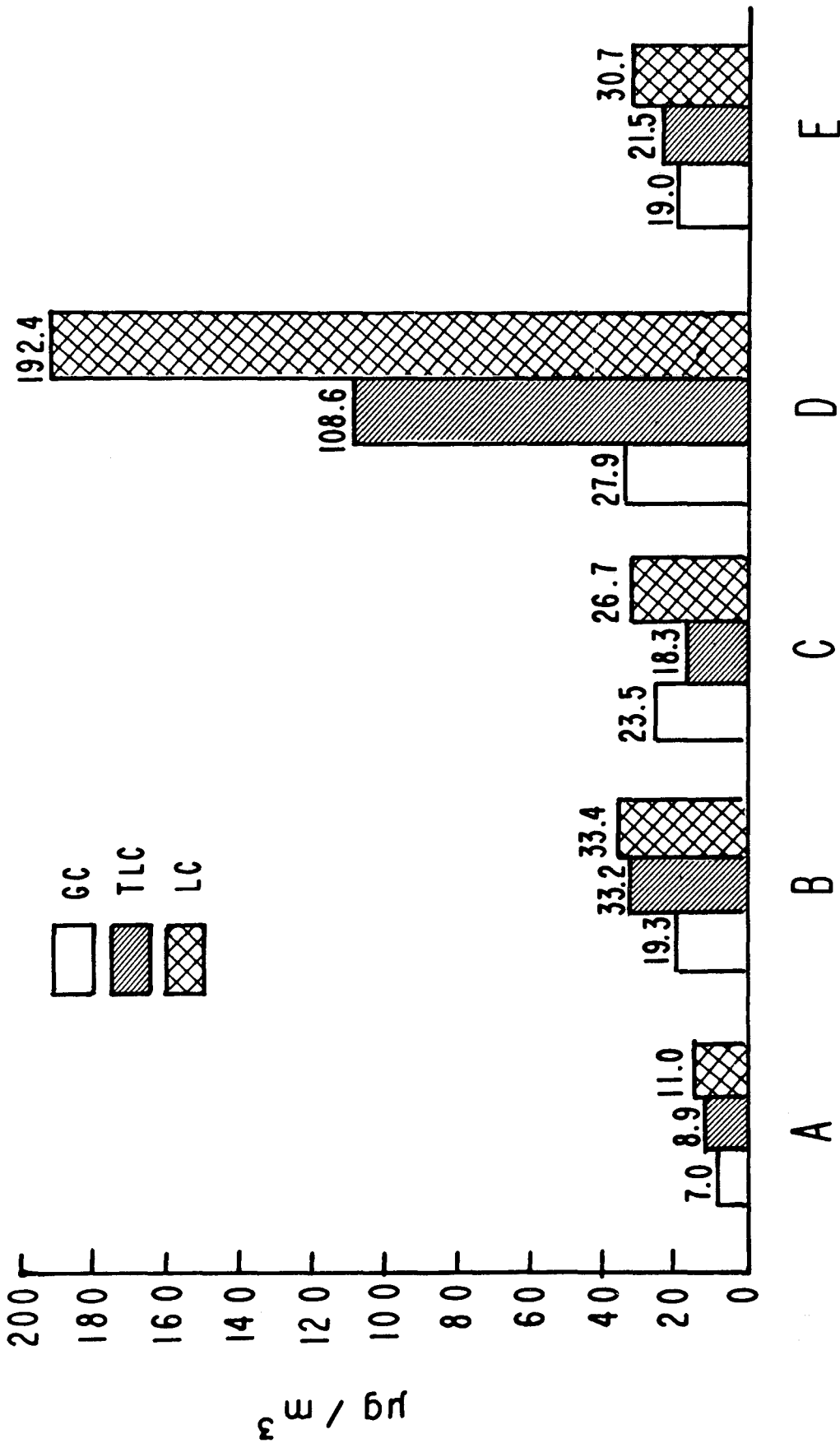


FIGURE 6. Rd I: BaP BY THREE METHODS



COMPANY

FIGURE 7. Rd II: BaP BY THREE METHODS

TABLE II. CORRELATION COEFFICIENTS:
BENZENE SOLUBLE VS. GC-UV AND TLC DATA

<u>Methods compared</u>	<u>Sampler used</u>	<u>Number of samples</u>		<u>Correlation coefficient</u>		<u>Student's t-Test for r=0 Probability</u>	
		<u>Rd-I</u>	<u>Rd-II</u>	<u>Rd-I</u>	<u>Rd-II</u>	<u>Rd-I</u>	<u>Rd-II</u>
B.S. vs. GC-UV	Hi-Vol	60	60	.581	.784	.0000	.0000
B.S. vs. GC-UV	Horizontal Elutriator	10	8	.726	.359*	.0175	.3832
B.S. vs. GC-UV	Gross	10	8	.383*	.791	.2746	.0193
B.S. vs. TLC	Hi-Vol	60	60	.713	.970	.0000	.0000
B.S. vs. TLC	Personal	144	148	.564	.635	.0000	.0000
B.S. vs. TLC	Horizontal Elutriator	10	9	.934	.884	.0001	.0016
B.S. vs. TLC	Gross	10	9	.818	.489*	.0038	.1815

*No significant difference from zero

TABLE III. COMPARISON OF METHODS
OF ANALYSIS FOR BENZO[A]PYRENE

<u>Methods compared</u>	<u>Number of samples</u>		<u>Correlation coefficient</u>		<u>Student's t-Test for r=0 Probability</u>	
	<u>Rd-I</u>	<u>Rd-II</u>	<u>Rd-I</u>	<u>Rd-II</u>	<u>Rd-I</u>	<u>Rd-II</u>
TLC vs. GC-UV	60	60	.536	.558	.0000	.0000
GC-UV vs. LC	60	60	.582	.479	.0000	.0001
TLC vs. LC	60	60	.776	.973	.0000	.0000

TABLE IV. MEAN CONCENTRATION OF 14 PNA's

<u>Sampler used</u>	<u>Average total concentration of 14 PNA's ($\mu\text{g}/\text{m}^3$)</u>	
	<u>Rd-I</u>	<u>Rd-II</u>
Hi-Vol	137.96	188.07
Personal	35.42	50.63
Horizontal Elutriator	106.31	118.75
Gross	91.22	116.38

TABLE V. COMPARISON OF THE TOTAL CONCENTRATION OF 14 PNA's
WITH THE TOTAL CONCENTRATION IN THE CARCINOGENIC SUBSET

<u>Sampler used</u>	<u>Number of samples</u>		<u>Correlation coefficient</u>		<u>Student's t-Test for r=0 Probability</u>	
	<u>Rd-I</u>	<u>Rd-II</u>	<u>Rd-I</u>	<u>Rd-II</u>	<u>Rd-I</u>	<u>Rd-II</u>
Hi-Vol	60	60	.956	.939	.0000	.0000
Personal	122	120	.931	.959	.0000	.0000
Horizontal Elutriator	20	18	.993	.869	.0000	.0000
Gross	20	18	.988	.944	.0000	.0000

TABLE VI. COMPARISON OF TRACE METAL CONCENTRATION
AND CONCENTRATION OF ORGANIC MATERIAL

<u>Trace metal conc. vs.</u>	<u>Correlation coefficient</u>		<u>Student's t-Test for r=0 Probability</u>	
	<u>Rd-I</u>	<u>Rd-II</u>	<u>Rd-I</u>	<u>Rd-II</u>
B.S. conc.	.146*	.270	.2794	.0382
14 PNA's (by GC-UV) conc.	.112*	.284	.4070	.0292
BaP (by TLC) conc.	.021*	.208*	.8745	.1137
BaP (by LC) conc.	.134*	.192*	.3222	.1456

*No significant difference from zero

REFERENCES

1. Hueper, W.C.: Occupational Tumors and Allied Diseases, p. 31, Charles C. Thomas, Baltimore (1942).
2. Lloyd, J.W.: Long Term Mortality Study of Steelworkers, V. Respiratory Cancer in Coke Plant Workers, J Occup Med, 13, No. 2, 53 (1971).
3. Fannick, N., L.T. Gonshor, and J. Shockley, Jr.: Exposure to Coal Tar Pitch Volatiles at Coke Ovens, Amer Ind Hyg Assoc J, 33, 461 (1972).
4. Federal Register, 37, No. 202, Oct. 18, 1972, Part 1910.
5. Chicago Tribune, October 31, 1969.
6. Jackson, G.W., P.D. Coulter, and B.A. Petro: Coal Tar Pitch Sampling Analysis, National Institute for Occupational Safety and Health, Final Report on Contract No. HSM-99-71-7, July 14, 1972.
7. Richards, R.T., A.T. Donovan, and J.R. Hall: A Preliminary Report on the Use of Silver Metal Membrane Filters in Sampling for Coal Tar Pitch Volatiles, Amer Ind Hyg Assoc J, 28, 590 (1967).
8. Greinke, R.A., P.D. Coulter, and B.A. Petro: Coal Tar Pitch Sampling Analysis, National Institute for Occupational Safety and Health, Final Report on Contract No. HSM-99-71-7, July 14, 1972.
9. Searl, T.D., F.J. Cassidy, W.H. King, and R.A. Brown: An Analytical Method for Polynuclear Aromatic Compounds in Coke Oven Effluents by Combined Use of Gas Chromatography and Ultraviolet Absorption Spectrometry, Anal Chem, 42, 954 (1970).
10. Lannoye, R.A., P.D. Coulter, B.A. Petro: Coal Tar Pitch Sampling Analysis, National Institute for Occupational Safety and Health, Final Report on Contract No. HSM-99-71-7, July 14, 1972.
11. Sawicki, E., T.W. Stanley, W.C. Elbert, and J.D. Pfaff: Application of Thin Layer Chromatography to the Analysis of Atmospheric Pollutants and Determination of Benzo[a]pyrene, Anal Chem, 36, 497 (1964).
12. Petro, B.A., P.D. Coulter: Coal Tar Pitch Sampling Analysis, National Institute for Occupational Safety and Health, Final Report on Contract No. HSM-99-71-7, July 14, 1972.
13. Intersociety Committee: Methods of Air Sampling and Analysis, p. 159, American Public Health Assoc., Washington, D.C. (1972).
14. Intersociety Committee: Methods of Air Sampling and Analysis, p. 173, American Public Health Assoc., Washington, D.C. (1972).

15. Jackson, G.W., P.D. Coulter, and B.A. Petro: Coal Tar Pitch Sampling Analysis, National Institute for Occupational Safety and Health, Final Report on Contract No. HSM-99-71-7, July 14, 1972.
16. Bottone, N.L., P.D. Coulter, and B.A. Petro: Coal Tar Pitch Sampling Analysis, National Institute for Occupational Safety and Health, Final Report on Contract No. HSM-99-71-7, July 14, 1972.
17. Greinke, R.A., P.D. Coulter, and B.A. Petro: Coal Tar Pitch Sampling Analysis, National Institute for Occupational Safety and Health, Final Report on Contract No. HSM-99-71-7, July 14, 1972.
18. White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel: A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere, Am Ind Hyg Assoc J, 31, 225 (1970).

APPENDIX A

Method 1.	PSM-1013	Soxhlet Extraction of Benzene Soluble Material in Airborne Particulates Trapped on Silver and/or Glass Fiber Filters.
Method 1.	PSM-1013a	Sampling and Soxhlet Extraction of Benzene Soluble Material in Airborne Particulates Trapped on Hi-Vol Filters (Glass Fiber).
Method 2.	PSM-1016	Gas Chromatographic and Ultraviolet Spectrophotometric Determination of Polynuclear Aromatic Compounds in Airborne Particulates.
Method 3.	PSM-1017	Fluorometric Determination of Benzo(a)Pyrene in Airborne Particulates after Thin Layer Chromatographic Separation.
Method 4.	PSM-1019	Liquid Chromatographic Separation and Spectrophotometric Determination of Polynuclear Aromatic Hydrocarbons in Airborne Particulates after Soxhlet Extraction.
Method 5.	PSM-1014	Composite Emission Index of Volatile Matter Collected on Air Sampling Filters.
Method 5.	PSM-1014a	Composite Emission Index of Volatile Matter Collected on Hi-Vol (Glass Fiber) Filters.
Method 6.	PSM-1020	Determination of Trace Metals in Airborne Particulates by Atomic Absorption Spectrophotometric Techniques.
Method 7.	PSM-1015	Gas Chromatographic Determination of Benzene, Toluene, Xylene, and Napthalene Adsorbed on Charcoal.
Standards	PSM-1018	Purification and Separation by Liquid Chromatography to Produce Ultrapure Compounds.

PARMA STANDARD TEST METHODS
UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM- 1013	ANALYSIS Benzene Solubles
RANGE 0.1 mg to > 100 mg	KEY REAGENT Benzene
PRECISION ±0.1 mg @ 1.0 mg range	MATRIX Air Particulates Trapped on Silver and/or Glass Fiber Filters
DATE ISSUED 10-29-71	DATE REVISED 1-14-72 e 700001

**SOXHLET EXTRACTION OF BENZENE SOLUBLE MATERIAL
IN AIRBORNE PARTICULATES TRAPPED ON SILVER
AND/OR GLASS FIBER FILTERS**

1. Purpose and Limitation

1.1. This method was designed for the determination of benzene soluble material in airborne particulates collected on silver and/or glass fiber filters by repeated extraction with hot benzene..

2. Principle of Method

2.1. The particulate material on the filter(s) is extracted by benzene, using the continuous cycling process of a Soxhlet extractor. After extraction the solution is filtered through the original filter(s).

2.2. The weight loss of the filter(s) is considered to be the amount of benzene solubles.

3. Apparatus and Reagents

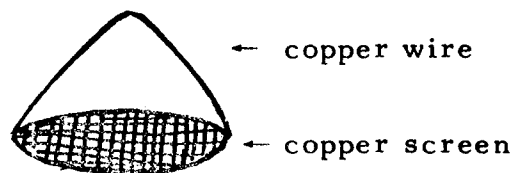
3.1. Apparatus

3.1.1. Soxhlet extractor apparatus - Six 250-ml size, Fisher Scientific, Catalog No. 9-551B or equivalent.

3.1.2. Extraction heater and support - Six positions, Fisher Scientific, Catalog No. 9-678 or equivalent.

3.1.3. Analytical balance - 0.01 mg sensitivity.

3.1.4. Copper basket - A copper basket is fabricated by cutting a copper screen (approximately 40 mesh) into 35-mm diameter circles. Two single strand copper wires are attached to the screen to form handles. This basket is used to support the filter(s) in the Soxhlet extraction chamber (see drawing).



3.1.5. Miscellaneous - Tweezers, 4 inch size and 10 inch size; aluminum tray, 9 x 12 inch; watch glasses, 2 1/2 inch diameter; microspatula; thin cotton gloves; 250-ml graduate; Carborundum boiling chips.

3.1.6. Filtering assembly - 500 or 1000-ml capacity suction flask; a fritted, 40-mm ID, coarse porosity, Pyrex Buchner funnel inserted into a rubber stopper (the appropriate size to fit the suction flask); a 38-mm OD glass ring, approximately 3 mm thick and approximately 12 mm tall. The glass ring is used to hold the filter(s) firmly on the fritted surface. This also prevents the filter from floating.

3.2. Reagents

3.2.1. Benzene - Spectroanalyzed grade.

3.2.2. Alconox and acetone - for preliminary cleaning of apparatus.

4. Procedure

4.1. Preliminary cleaning of Soxhlet extractor glassware.

4.1.1. Using a solution of Alconox in water, wash each part of the Soxhlet extractor. Rinse thoroughly with distilled water. Dry the outside of each part with a lint-free tissue. Dry the inside by rinsing with acetone. Air dry to remove the excess acetone.

4.1.2. Add 180 ml of benzene and 5 to 10 boiling chips to each extraction flask. Assemble the Soxhlet extractor. Place the copper basket in the extractor. Apply heat and continue heating for 2.5 hours after the slowest Soxhlet extractor cycles for the first time.

4.1.3. Turn off the heat and discard the benzene and boiling chips.

(Benzene should be discarded in waste solvent can.)

4.2. Sample procedure - Samples are usually analyzed in lots of six.

4.2.1. Check for sample labeling on the bottom portion of the cassettes containing the samples. Relabel if necessary. Remove the tops from the cassettes. Expose the samples to room conditions for 1 hour. This process equilibrates the moisture content of the filter(s).

4.2.2. Using the small tweezers and microspatula, remove all the filters above the bottom support filter. The number and type of filters may vary. A silver filter usually is located next to the filter support. Once removed from the cassette, the silver filter is used both as a sample and as a support for the other filters. If a silver filter is not contained in the cassette, use a silver filter previously extracted in the Soxhlet extractor. Using tweezers, place the filter(s) directly on the balance pan. Weigh and record the filter(s) weight to the nearest 0.01 mg. Remove filter(s) and place on a numbered watch glass. Repeat for each sample.

4.2.3. Place 180 ml of benzene and 5 to 10 boiling chips in each extraction flask.

4.2.4. Carefully transfer the filter(s) to the copper basket. Using the large tweezers, lower the basket into the Soxhlet chamber. Assemble Soxhlet apparatus. Repeat for each sample. This portion of the procedure may be performed the day prior to extraction.

4.2.5. Turn the heaters on maximum setting. Extract for 2.5 hours after the slowest Soxhlet extractor cycles once.

4.2.6. Turn the heaters off. Samples may or may not be filtered immediately.

4.2.7. Assemble the filtering apparatus in well-ventilated hood. Connect the filtering apparatus to suction. Remove the extraction chamber and flask, while still assembled, from the heater. Tilt the entire assembly in order to drain as much benzene as possible from the extraction chamber into the extraction flask. Using the large tweezers, rer

the copper basket containing the filter(s) from the Soxhlet chamber. Using the small tweezers, carefully mount the filter(s) on the filtering apparatus. Using the small tweezers, lower the glass ring on to the silver filter. Using a benzene washing bottle, rinse the Soxhlet chamber at least three times. Pour the washings into the filtering funnel. Care should be taken to remove from the Soxhlet chamber all insoluble particles that may have been removed from the filter. Continue filtering the entire contents of the extraction flask (minus the boiling chips) through the filtering funnel. Rinse extraction flask three times with benzene. Add the washings to the filtering funnel.

4.2.8. Using small tweezers, remove the filter(s) and place on a numbered watch glass. Repeat paragraph 4.2.7. for each sample. Air dry all the samples for 1 hour after the last sample is filtered.

4.2.9. Using small tweezers, place the filter(s) directly on the balance pan. Weigh to the nearest 0.01 mg. Record weight.

5. Calculation

$$(A - B) (1000) = C$$

where

A = Weight of filter(s) before extraction, g (Paragraph 4.2.2.)

B = Weight of filter(s) after extraction, g (Paragraph 4.2.9.)

C = Benzene soluble, mg.

Report to the nearest 0.1 mg.

6. References

6.1. R. T. Richards, D. T. Donovan, and J. R. Hall, Amer. Ind. Hyg. Assoc., J., 28, 590 (1967).

6.2. Parma Technical Center - Notebook 572-5.

PARMA STANDARD TEST METHODS
UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM- 1013a	ANALYSIS Benzene Solubles
RANGE 5.0 mg to 5.0 g	KEY REAGENT Benzene
PRECISION ±5 mg @ 200 mg level	MATRIX Airborne Particulates Trapped on Hi-Vol (Glass Fiber) Filters
DATE ISSUED 6/1/72	DATE REVISED 6 700001

SAMPLING AND SOXHLET EXTRACTION OF BENZENE
SOLUBLE MATERIAL IN AIRBORNE PARTICULATES
TRAPPED ON HI-VOL FILTERS (GLASS FIBER)

(This procedure utilizes PSM-1013)

1. Purpose and Limitation

1.1. This method is designed for the determination of benzene soluble material in airborne particulates collected on Hi-Vol (glass fiber) filters by repeated extraction with hot benzene. The Hi-Vol filters contain a large quantity of particulate matter. This requires a modification of PSM-1013.

1.2. The data from the benzene solubles may be used as a guideline for various other analyses of the particulates trapped on the Hi-Vol filters. The sampling procedure of the Hi-Vol filters is outlined in this method.

2. Principle of Method

2.1. The filters are divided in four portions, the portions are weighed, and a total weight (filter plus sample) is determined from a sum of the parts. The separate portion weights are recorded and used in the calculations.

2.2. The portion of the filter, used for the benzene extraction, is placed in a glass crucible before inserting in the Soxhlet chamber.

2.3. See PSM-1013, section 2. (Principle of Method).

2.4. The benzene extract is divided and used for PSM-1017 and PSM-1019. These samples are stored in a freezer away from heat and light to inhibit deterioration.

2.5. The remaining portions of the filter are reserved for other as described in various PSM's.

3. Apparatus and Reagents

3.1. Apparatus

3.1.1. See PSM-1013, paragraphs 3.1.1., 3.1.2., and 3.1.3.

3.1.2. Glass Crucibles, Gooch type, high form, 30-ml capacity, coarse porosity - available from Fisher Scientific Cat. No. 8-237-A. Label the crucibles using "De-Cal" available from Del-Craft, U.S.A., Inc., Rt. 309, Hatfield, Pennsylvania 19440, according to instructions.

3.1.3. Drying Oven - 100°C such as Fisher Scientific Cat. No. 13-244-1 or equivalent.

3.1.4. Muffle Furnace - Temco Model No. F-1740 or equivalent - for cleaning glass crucibles.

3.1.5. Indicating Pyrometer Controller for Furnace - Capable of regulating $\pm 20^{\circ}\text{C}$ at 600°C . Available from Fisher Scientific Co., Cat. No. 10-557-13.

3.1.6. Copper, Wire Screen (approximately 40 mesh) - Cut in circles with a 35-mm diameter.

3.1.7. Desiccator - plain - 100-150-mm diameter containing indicating desiccant, Fisher Scientific Co., Cat. No. 8-636 or equivalent.

3.1.8. Freezer - Storage Cabinet - Available from Fisher Scientific Co., Cat. No. 13-988-30 or equivalent.

3.1.9. Miscellaneous - Clean metal scissors (to avoid metal contamination) or if available plastic scissors; crucible tongs; furnace tongs; aluminum tray, 9 x 12 inch; tweezers, 10 inch size; thin cotton gloves; two 250-ml graduates; Carborundum boiling chips; six 250-ml beakers, with covers; 12 glass bottles, wide-mouth approximately 200-ml capacity; plastic washing bottle, 500-ml capacity; large lint-free tissue, "Super-Wipes" available from Sorg Products or equivalent; and asbestos sheets, approximately 12-inch squares.

3.2. Reagents

3.2.1. See PSM-1013, paragraph 3.2.

4. Procedure

4.1. Preliminary cleaning of glassware.

4.1.1. Glass Crucibles

4.1.1.1. Place the glass crucibles in the 600°C muffle furnace for 1 hour. Decrease furnace temperature to 250°C . Once the 250°C temperature is reached, remove the crucibles from the furnace using the furnace tongs. Place on a clean piece of asbestos to cool. After cooling, place the crucibles in the desiccator.

4.1.2. Soxhlet extractor

4.1.2.1. See PSM-1013, paragraph 4.1.1.

4.1.2.2. Add 180 ml of benzene and 5 to 10 boiling chips to each extraction flask. Place a copper circle and a glass crucible in each extraction chamber. (Assemble the Soxhlet extractor.) Apply heat and continue heating for 2.5 hours after the slowest Soxhlet extractor cycles for the first time.

4.1.2.3. Turn off the heat. In a well-ventilated hood, disassemble the Soxhlet extractor. Using the tweezers, remove the glass thimble from the chamber. Place the crucible in an aluminum tray (lined with a Super-Wipe). Discard the benzene and boiling chips from the extraction flask.

4.1.2.4. Air dry the glass crucibles for 1 hour in the hood.

4.1.2.5. Repeat paragraph 4.1.1.1. Soxhlet and glass crucibles are now ready for use.

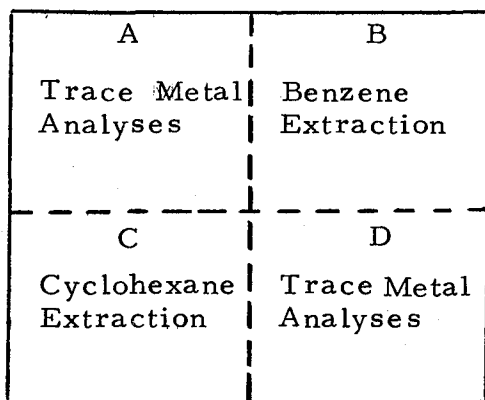
4.2. Division and Distribution of Hi-Vol Filter - Samples are usually extracted in lots of six.

4.2.1. Collect the following apparatus: six 250-ml beakers, that have been cleaned according to PSM-1020; six glass crucibles (stored in desiccator); six aluminum thimbles, that have been cleaned according to PSM-1014a; weight sheet, [see Appendix Figure 1.]; and 12 glass bottles labeled with the appropriate sample numbers.

4.2.2. While wearing thin cotton gloves, remove the sample folder from the envelope. Open the folder and flatten along the crease. Open the Hi-Vol filter. See diagram below.

Hi-Vol Filter

1.



1. Original fold

2. Cutting line

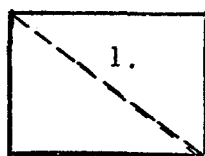
Figure 2.

4.2.3. Cut the sample in two parts along the original fold. Cut into four parts along indicated cutting line.

4.2.4. Portions A and D are combined for trace metal analyses and both are placed directly on the balance pan. Weigh to the nearest 0.1 mg. Record weight on weight sheet in area designated for trace analyses.

4.2.5. If portions A and D weigh less than 1.9 g proceed according to paragraph 4.2.7.

4.2.6. If portions A and D of the filter weigh more than 1.9 g, divide portions B and C as in Figure 3.



Portions B and C
1. Cutting line

Figure 3.

Place one-half of B and one-half of C along with portions A and D directly on the balance pan, reweigh to the nearest 0.1 mg. Record the weight on the weight sheet in the area designated for trace metal analyses. While holding the filter over the appropriate 250-ml beaker, carefully fold the filter and place in the beaker. Set aside for trace metal analyses according to PSM-1020.

4.2.7. Place portion C directly on the balance pan, weigh to the nearest 0.1 mg. Record the weight on the weight sheet in area designated for cyclohexane extraction. While holding the filter over the alundum thimble, paragraph 4.2.1., fold the filter and insert in the thimble. Set aside for cyclohexane extraction according to PSM-1014a.

4.2.8. Weigh the glass crucible (paragraph 4.2.1.) to the nearest 0.1 mg. Record the weight along with the crucible number.

4.2.9. Carefully fold portion B and insert in the crucible. Reweigh to the nearest 0.1 mg. Record the weight of the sample, filter, plus the crucible. Set aside for the benzene extraction.

4.2.10. Repeat paragraphs 4.2.2. through 4.2.9. for each sample.

4.3. Extraction

4.3.1. Place 180 ml of benzene and 5 to 10 boiling chips in each extraction flask.

4.3.2. Use the tweezers to lower the glass crucible containing the sample (paragraph 4.2.9.) into the Soxhlet chamber. Assemble the Soxhlet apparatus. Repeat for each sample. This portion of the procedure may be performed the day prior to extraction.

- 4.3.3. Turn the heaters on maximum setting. Extract for 2.5 hours after the slowest Soxhlet extractor cycles once. Turn the heaters off. Samples may or may not be removed immediately. Samples should not sit in the extractor more than one hour.
- 4.3.4. Remove the extraction chamber and flask from the heater while still assembled. Tilt the entire assembly in order to drain as much benzene as possible from the extraction chamber into the extraction flask. After the benzene has drained from the crucible, use the tweezers to remove the crucible from the chamber. This should be done in a well-ventilated hood. Place the crucible in an aluminum tray lined with a "Super Wipe." Store in the hood to air dry.
- 4.3.5. Use a benzene washing bottle to rinse the Soxhlet chamber at least three times. Pour the washings into a 250-ml graduate. Transfer the entire contents of the extraction flask (minus the boiling chips) to the same graduate. Rinse the extraction flask at least three times with benzene. If color persists, continue rinsing until washings are clear. Add the washings to the same graduate. Measure the volume. Transfer one-half of the solution to the appropriate previously labeled bottle for thin layer chromatography (See PSM-1017). Transfer the remaining solution to a bottle previously labeled for liquid chromatography (See PSM-1019). Rinse the graduate four times with small portions of benzene dispensed from the washing bottle. Transfer two rinsings to each bottle. Place aluminum foil over each bottle and cap. When cool, store liquid chromatography and thin layer chromatography samples in the freezer.
- 4.3.6. Repeat paragraphs 4.3.4. and 4.3.5. for each sample.
- 4.4. Weighing of benzene solubles
- 4.4.1. Air dry the glass crucibles containing the samples in a hood until the unexposed portion of the filter is opaque, approximately 1 hour.
- 4.4.2. Use the crucible tongs to place the crucibles in the 100°C drying oven for 1 hour. With the tongs, remove the crucibles from the drying oven and place in the desiccator for cooling. Cool for 2 hours. Weigh to the nearest 0.1 mg and record weight.
- 4.5. Cleaning of Glass Crucibles for Re-use
- 4.5.1. Discard the sample. By using a compressed air line remove as many of the particulates as possible.

4.5.2. Repeat paragraph 4.1.1.1.

5. Calculation

5.1. Weight sheet (Figure 1.)

5.1.1. Sample weight of benzene extraction

$$E - F = G$$

where

E = Weight of sample, filter, plus glass crucible, g.
(paragraph 4.2.9.)

F = Weight of glass crucible, g. (paragraph 4.2.8.)

G = Weight of the filter and sample used for benzene extraction, g.

5.1.2. Record the weight of benzene extraction portion (calculation G) in the designated area on the weight sheet. (Column 4)

5.1.3. Add each row for each sample and record in the total weight column. (Column 6)

5.1.4. Reproduce 5 copies, distribute one for each type of analysis.

Mark the following weight sheets "one-half;" thin layer chromatography, (column 4), liquid chromatography, (column 4), emission index, (column 5), and gas chromatography, (column 5).

5.2. Benzene Solubles

5.2.1. Factor for benzene soluble

$$\frac{H}{G} = J$$

where

G = Weight of the filter used for benzene extraction, g,
(paragraph 5.1.1., weight sheet column 4).

H = Total weight of filter, g, (paragraph 5.1.3., weight sheet column 6).

J = Factor

5.2.2. Total benzene solubles

$$(E - L) \times J \times 1000 = M$$

where

E = Weight of the sample, filter plus the crucible before extraction, g, (paragraph 4.2.9.).

L = Weight of the sample, filter plus the crucible after extraction, g, (paragraph 4.4.2.).

J = Factor (paragraph 5.2.1.).

M = Milligrams benzene solubles in entire filter.

6. References

6.1. Parma Technical Center Notebook 572-5 and 572-9.

PARMA STANDARD TEST METHODS
UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM- 1016	ANALYSIS Polynuclear Aromatics
RANGE 0 to 500 µg each of all components	INSTRUMENT Gas Chromatograph
PRECISION Not Determined Estimated at ± 30% at all levels	MATRIX Polynuclear Aromatics Trapped on Membrane Filters
DATE ISSUED 2/22/72	DATE REVISED 0700142

**GAS CHROMATOGRAPHIC AND ULTRAVIOLET SPECTROPHOTOMETRIC
DETERMINATION OF POLYNUCLEAR AROMATIC COMPOUNDS
IN AIRBORNE PARTICULATES**

(This procedure utilizes PSM-1014 or PSM-1014a)

1. Purpose and Limitations

1.1. This method is designed for gas chromatographic and ultraviolet spectrophotometric determination of the polynuclear aromatic compounds: fluoranthene, pyrene, benz(c)acridine, chrysene, benz(a)anthracene, benz(a)anthrone, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)-fluoranthene, benzo(e)pyrene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, and anthanthrene. The method could be expanded to include other polynuclear compounds.

1.2. Other compounds trapped on the filters which have the same gas chromatographic retention time as these compounds may interfere in the subsequent ultraviolet analysis.

1.3. Compounds eluting with the internal standard, o-terphenyl, may also impair the accurate ultraviolet or gas chromatographic measurement of o-terphenyl.

2. Principle of Method

2.1. The polynuclear aromatic compounds are extracted from the trapped airborne particulates contained on the filter with cyclohexane using a Soxhlet extractor.

2.2. After the addition of an internal standard, the extract is evaporated to approximately 30 µl, and a portion is injected into a gas chromatogr

2.3. The polynuclear compounds and the internal standard are trapped as they elute from the chromatograph.

2.4. The ultraviolet absorption spectra of the trapped compounds provide a quantitative measurement.

3. Apparatus, Reagents, and Gas Chromatographic Column

3.1. Apparatus

3.1.1. Gas Chromatograph - F & M Model 810 or equivalent, equipped with a flame ionization detector and effluent splitters (10 to 1 ratio). The smaller portion of the effluent flows to the flame ionization detector. The larger portion flows into a trapping assembly.

3.1.1.1. Gas Chromatographic Trapping Assembly - The design of this trapping assembly is shown in Figure 1. The trapping assembly is located next to the flame ionization detector. If the F & M 810 chromatograph is also equipped with a thermal conductivity detector, it must be removed in order to allow space for the trapping assembly. The traps are stainless steel tubing, 3/16 inch O.D., and 12 inches long. Firmly attach a Swage nut and ferrules to one end of the trap. Place a rubber O ring over the tubing to hold the Swage nut in place. The Swage nut will provide a grasping handle and will aid in removing the trap from the instrument during the run. Ten traps are required for each analysis. Store the traps in a rack with ten numbered slots (see Figure 2). Each number on the rack will correspond to specific polynuclear compound(s). In several cases, more than one polynuclear compound will be trapped in a trap, because of incomplete gas chromatographic separation. Drill holes into the base of the rack, for placement of the ultraviolet cells. Adjust the height of the rack to allow the base of the 3/16 inch trap tubing to fit into the top portion of the ultraviolet cell. This will allow the polynuclear compounds to be washed directly into the 10 mm ultraviolet cells with cyclohexane.

3.1.2. Recorder - 1 mv. sensitivity, Texas Instruments Model No. PS02-6A or equivalent.

3.1.3. Integrator - Hewlett Packard Model 3370A or equivalent.

3.1.4. Recording Spectrophotometer - Applied Physics Corporation, Cary Model 14 or equivalent, equipped with rectangular 10 mm far ultraviolet (UV) silica cells.

3.1.5. Rectangular Far Ultraviolet Silica Cells - 10 mm path, with stopper - such as Beckman Instruments, Inc., Catalog No. 75191 or

equivalent. Calibrate cells at 1.0 ml and at 3.0 ml with cyclohexane.

3.1.6. Tubing - Stainless steel, 1/8 inch O.D., 20 foot length 0.02 inch wall thickness.

3.1.7. Tubing - Stainless steel, 3/16 inch O.D. - 12 inch lengths, 10 traps are required for each sample.

3.1.8. Swage Connectors - Four 1/8 inch nuts with ferrules (for the gas chromatographic columns); 3/16 inch nut with ferrules, one set for each trap.

3.1.9. Analytical Balance - Single pan type, 0.01 mg sensitivity.

3.1.10. Glassware - One 10- μ l Hamilton Syringe; one 100- μ l Hamilton Syringe; 2-ml syringe; one large glass evaporating tray, 6 inches by 12 inches; 4.0 ml capacity (one dram) glass vials, one for each sample; 250-ml beakers or glass bottles of similar volume for evaporation of the Soxhlet extracts, one for each sample; 10-ml beaker.

3.1.11. Miscellaneous - silanized glass wool, spatula, gas chromatographic column funnel.

3.1.12. Hot plate - about one sq. ft., fast response with stepless control from 20°C to 100°C - Corning Model - Fisher Scientific Catalogue No. 11-495-20.

3.2. Reagents

3.2.1. Chloroform, methylene chloride and toluene - all reagent grade.

3.2.2. Cyclohexane - spectranalyzed, available from Fisher Scientific.

3.2.3. Polynuclear Standards - o-terphenyl, bibenzyl, fluoranthene, pyrene, benz(c)acridine, chrysene, benz(a)anthracene, benz(a)anthrone, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, and anthanthrene - obtained from Eastman Kodak and other supply houses. Each compound was checked for purity by gas chromatography, and by comparison with infrared and ultraviolet reference spectra. Impure compounds were purified by liquid chromatography (see PSM-1018).

3.2.4. Internal standard o-terphenyl, 1 μ g/ μ l - to the nearest 0.1 mg, weigh 0.1000 gms of o-terphenyl in a tared 10-ml beaker. Transfer quantitatively from the beaker to a 100-ml volumetric flask with toluene. Dilute to the mark with toluene. O-terphenyl was obtained from Aldrich Chemical Co.

3.2.5. Internal standard bibenzyl, 1 $\mu\text{g}/\mu\text{l}$ - to the nearest 0.1 mg, weigh 0.1000 gms of bibenzyl in a tared 10-ml beaker. Transfer quantitatively to a 100-ml volumetric flask with toluene. Dilute to the mark with toluene. Bibenzyl was obtained from Eastman Kodak Co.

3.2.6. Dexsil 300 GC - available from Analabs, Inc., a gas chromatographic supplier.

3.2.7. Chromosorb G, AW, DMCS Treated, 80-100 mesh - available from gas chromatographic suppliers.

3.3. Gas Chromatographic Column - 10 ft x 1/8 inch O.D. stainless steel tubing packed with 3% by weight Dexsil 300 GC on Chromosorb G, AW, DMCS Treated, 80-100 mesh.

3.3.1. Support Preparation - Add 3.0 grams of Dexsil 300 GC to a 250-ml beaker. Dissolve in a mixture of 100 ml of chloroform and 100 ml of methylene chloride. Add this solution to 100 grams of the Chromosorb G, AW, DMCS Treated 80-100 mesh which has been spread out in the glass evaporating tray. Allow the solvent to evaporate in a hood. Occasionally stir gently with a spatula. Place on a hot plate and apply gentle heat (about 40°C) in order to remove the last traces of the solvents. Store the coated support in a clean bottle.

3.3.2. Column Packing - Cut the stainless steel tubing into two 10.0 ft lengths. Clean the inside of the tubing with acetone to remove any oil deposits. Completely dry the tubing by passing compressed air through the tubing. Cap one end of each column with an end cap. With the aid of a funnel slowly pour the coated support (paragraph 3.3.1.) into the stainless steel tubing. While adding the support, hold the tube in an upright position and vibrate the column gently by tapping to obtain a uniform packing. When the column is completely filled, remove approximately 1/4 inch of support from each end and completely fill these voids with silanized glass wool. Firmly attach a Swage nut and ferrules to each end of each column. Coil the columns so they will fit into the oven section of the chromatograph (approximately 10 inch diameter).

3.3.3. Column Conditioning - Place both columns into the oven, connecting the front end of the column to the injection port. Do not connect the end of the column to the splitter. Bake the columns at 350°C overnight with a low helium flow (approximately 20 cc/min.). Connect the columns to the splitter after the overnight bake.

4. Procedure

4.1. Gas Chromatographic Parameters (F & M 810)

4.1.1. Column Temperature - 180°C initial temperature, then program to 350°C at 6°C/min. Hold at 350°C for 12 minutes.

4.1.2. Detector Temperature - 350°C.

4.1.3. Injection Port Temperature - 340°C - Temperatures above 350°C may cause decomposition of the polynuclear compounds.

4.1.4. Carrier Gas - helium.

4.1.5. Carrier Gas Flow - 40 cc/min.

4.1.6. Hydrogen Flow - about 60 cc/min. (50 psi).

4.1.7. Air Flow - about 400 cc/min. (50 psi).

4.1.8. Sample Injection Volume - approximately 8 µl.

4.1.9. Approximate Retention Times

<u>Compound</u>	<u>Retention Times (min.)</u>
bibenzyl	5.0
o-terphenyl	11.0
fluoranthene	15.6
pyrene	17.1
benz(c)acridine	22.0
chrysene	23.0
benz(a)anthracene	23.0
benz(a)anthrone	25.0
benzo(b)fluoranthene	28.5
benzo(j)fluoranthene	28.5
benzo(k)fluoranthene	28.5
benzo(e)pyrene	30.6
benzo(a)pyrene	30.6
dibenz(a, h)anthracene	36.0
anthanthrene	38.3
benzo(g, h, i)perylene	38.3

4.1.10. Total elution time - 41 minutes.

4.2. Integrator Parameters (Hewlett Packard 3370A).

4.2.1. Noise Suppression - 3

4.2.2. Up Slope Sensitivity-0.03

4.2.3. Down Slope Sensitivity-0.03

4.2.4. Baseline Delay-0.1

4.2.5. Front Shoulder - ON

4.2.6. Rear Shoulder-1000

4.2.7. Peak Summation-1000

4.3. Spectrophotometer parameters (Cary 14)

4.3.1. Instrument parameters for UV range 200-350 nm.

4.3.1.1. Scan Speed - 10 Å/sec.

4.3.1.2. Chart - On

4.3.1.3. Pen - On

4.3.1.4. Slit - On

4.3.1.5. Slit Control - 25

4.3.1.6. Source - UV

4.3.1.7. IR detector - Out

4.3.1.8. Selector - UV

4.3.1.9. Shift Knob - Out

4.3.2. Instrument parameters for visible range, 350-600 nm.

4.3.2.1. See paragraphs 4.3.1.1. through 4.3.1.5. (same parameters as UV range).

4.3.2.2. Source - Vis

4.3.2.3. IR detector - Out

4.3.2.4. Selector - Vis

4.3.2.5. Shift Knob - Out

4.4. Preparation of Polynuclear Standard Solutions

4.4.1. To the nearest 0.01 mg, weigh directly into individual tared 25-ml volumetric flasks 3 to 5 mg of each analyzed polynuclear compound (Table I) and the internal standard, o-terphenyl. Dilute each flask (15 flasks) to volume with cyclohexane.

4.4.2. By using the following equation, transfer the appropriate aliquots, (Q), of each standard solution to four 50-ml volumetric flasks, to obtain concentrations of 1.0, 2.0, 4.0, and 8.0 µg/ml. Dilute the 50-ml volumetric flasks to volume with cyclohexane.

$$\frac{1.25 \times R}{W} = Q$$

where W = polynuclear sample weight, mg (paragraph 4.4.1.).

R = desired concentration (1.0, 2.0, 4.0, and 8.0 µg/ml)
in 50-ml volumetric flasks, (paragraph 4.4.2.).

Q = aliquot (ml) taken from 25-ml volumetric flask
to obtain the desired concentration.

(NOTE: Because chrysene and benz(a)anthracene are strong ultraviolet absorbers, the desired concentrations, R, of these standard solutions are 0.5, 1.0, 2.0 and 4.0 µg/ml.)

4.4.3. By using the ultraviolet spectrophotometer and the conditions of compound analysis indicated in Table I, determine the peak height, P, at the maximum wavelength (Table I, column 3) for all calibration standard solutions (paragraph 4.4.2. - 4 solutions for each compound). Use cyclohexane in the 10-mm reference cell. The peak height values are determined by using the "baseline" method: a straight line is drawn on the curve between the specified wavelengths (Table I, column 4). The height of the peak at the "maximum wavelength" (Table I, column 3) is measured from the baseline (see Figure 3a for an example).

TABLE I
Conditions for Ultraviolet Analysis

<u>Compound</u>	<u>Trap No.</u>	<u>Maximum Wavelength (nm)</u>	<u>Baseline or Background (nm)</u>
o-terphenyl	1	235	249
fluoranthene	2	288	284 - 292
pyrene	3	336	327 - 345
benz(c)acridine	4	384	380 - 392
chrysene	5	267	260 - 275
benz(a)anthracene	5	289	297
benz(a)anthrone	6	378	420
benzo(b)fluoranthene	7	302	297
benzo(j)fluoranthene	7	332	328 - 337
benzo(k)fluoranthene	7	402	397 - 408
benzo(e)pyrene	8	332	325 - 338
benzo(a)pyrene	8	384	398
dibenz(a, h)anthracene	9	221	218 - 228
benzo(g, h, i)perylene	10	362	351 - 372
anthanthrene	10	430	442

If only one wavelength value is given in Table I, column 4, the horizontal baseline approach is employed: a horizontal line is drawn on the curve at the specified background wavelength (Table I, column 4) and the height of the peak at the "maximum wavelength" is measured from the baseline (see Figure 3b).

4.5. Sample Preparation and Analysis

4.5.1. Extract the sample filter for 5 hours by refluxing with 200 ml of cyclohexane in a Soxhlet extractor. During the extraction the Soxhlet is covered with aluminum foil to protect the sample from light. (See PSM-1014 and PSM-1014a for the extraction procedure.)

4.5.2. Low Concentration (Sample in the vial-paragraph 4.5.3.-will appear pale yellow to light brown.) After the extraction, transfer the extract to a 250-ml beaker and, with a 100- μ l Hamilton Syringe, add exactly 40 μ l (40 μ g) of the internal standard, o-terphenyl (reagent 3.2.4.). In a hood evaporate the contents of the beaker to dryness. Add a small portion of toluene (around 0.5 ml) to the beaker, swirl to dissolve the residue, and transfer quantitatively to a 1 dram vial. Rinse the beaker with very small additional portions of toluene and transfer the washings to the one dram vial.

4.5.3. Evaporate the contents of the one dram vial to approximately 30 μ l. If necessary add additional toluene to the vial to reach approximately 30 μ l. (As a guide, add 30 μ l of cyclohexane to another vial in order to judge the sample volume.)

4.5.4. Inject approximately 8 μ l of this solution into the chromatograph using the GC parameters given in paragraph 4.1. It is not necessary to record this volume.

4.5.5. Insert the stainless steel traps in the trapping assembly as the desired compounds elute. The approximate times for insertion and removal of the stainless steel traps are ascertained by injecting into the chromatograph a synthetic solution containing all the polynuclear compounds and the internal standard, o-terphenyl. These times may vary slightly from sample to sample; therefore, observe the chromatogram in order to coordinate the insertion and removal of the trap at the precise elution of the compound. The compounds present in each of the 10 traps are given in Table I, columns 1 and 2.

4.5.6. A typical chromatogram of a synthetic containing all the compounds is illustrated in Figure 4. A chromatogram of a typical sample is illustrated in Figure 5. Proceed with the ultraviolet determination of the trapped compounds as described in paragraph 4.5.8.

4.5.7. High Concentration (Sample in the vial will appear dark brown or black.) Hi Vol filters commonly contain large amounts of polynuclear aromatic compounds. Interferences with the ultraviolet measurem

the internal standard, o-terphenyl, may occur whenever large amounts of PNA's are present. To circumvent this difficulty, use the following steps.

4.5.7.1. Inject exactly 15 μ l (15 μ g) of o-terphenyl (reagent 3.2.4.) and bibenzyl (reagent 3.2.5.) into the chromatograph. Using the integrator parameters in paragraph 4.2., obtain and record the number of counts for each internal standard. Caution: Once these counts have been obtained, do not adjust the helium, air or hydrogen flows to the flame ionization detector. Also, note and use the same attenuator settings for subsequent samples. If the flow settings have been changed, repeat the 15 μ l internal standard injection, obtain and record the integrator counts.

4.5.7.2. Sample Preparation - After extraction (paragraph 4.5.1.), add exactly 80 μ g (80 μ l) of o-terphenyl (reagent 3.2.4.) and exactly 80 μ g (80 μ l) of bibenzyl (reagent 3.2.5.) to the 250-ml beaker, and continue as indicated in paragraphs 4.5.2. and 4.5.3.. Because of the large concentration of polynuclears in these samples, adjust the final volume in the one dram vial from 60 to 80 μ l.

4.5.7.3. Sample Analysis - Inject approximately 8 μ l of the sample into the chromatograph, using the gas chromatographic parameters given in paragraph 4.1. and the integrator parameters given in paragraph 4.2.. Record the integrator counts of the two internal standards. See paragraph 4.1.9. for the approximate retention times. Trap the desired compounds as described in paragraph 4.5.5.. Proceed with the ultraviolet measurement of the trapped compounds as described in paragraph 4.5.8..

4.5.8. Insert the nozzle of a plastic wash bottle containing cyclohexane in the top of the trap placed in the rack (Figure 2.). Rinse the trap with small increments of cyclohexane. Catch the rinsings in the far ultraviolet silica cell previously calibrated to 3.0 ml. Dilute to 3.0 ml with cyclohexane.

4.5.9. Obtain the peak height as described in paragraphs 4.3. and 4.4.3..

4.5.10. If the concentration in the cell is too high (recorder pen on the spectrophotometer goes off scale at the maximum wavelength of the analyzed compound) dilute the sample. With a syringe, remove 2.0

of the sample from the cell and dilute the remaining 1.0 ml to 3.0 ml with cyclohexane. Repeat this dilution technique until the recorder pen is on scale. Record the number of dilutions, n.

4.5.11. Repeat paragraphs 4.5.8. through 4.5.10. for the other polynuclear compounds and the internal standard in the traps.

5. Calculations:

5.1. Ultraviolet Slope Factors

5.1.1. Divide the concentration, $\mu\text{g/ml}$ (R, paragraph 4.4.2.), by the measured peak height (P, paragraph 4.4.3.) obtained for the four calibration mixtures of each component.

5.1.2. Determine the average ultraviolet slope factor (S) for each analyzed polynuclear compound and the internal standard. A typical calculation is illustration below:

benzo(k)fluoranthene

Conditions: cyclohexane reference cell; maximum wavelength, 402 nm; baseline, 397 to 408 nm.,

<u>Peak height (P)</u>	<u>Concentration $\mu\text{g/ml}$ (R)</u>	<u>Slope Factor R/P</u>
.840	8.0	9.52
.416	4.0	9.63
.211	2.0	9.48
.105	1.0	<u>9.52</u>

Average Slope Factor, S 9.54

5.2. Integrator Internal Standards Slope Factors

$$\frac{X}{15 \mu\text{g}} = O,$$

$$\frac{Y}{15 \mu\text{g}} = B$$

where X = integrator counts for o-terphenyl (paragraph 4.5.7.1.).

Y = integrator counts for bibenzyl (paragraph 4.5.7.1.).

O = slope factor for o-terphenyl, counts/ μg .

B = slope factor for bibenzyl, counts/ μg .

5.3. Internal Standard Recovery Factor (by Ultraviolet Spectroscopy)

If no interferences are evident in the ultraviolet spectrum, calculate the recovery factor (R) of the internal standard, o-terphenyl, by ultraviolet spectroscopy.

$$\frac{A}{P_{is} S_{is}} = R_{uv}$$

where $A = \mu\text{g}$ of o-terphenyl added to the extraction,
(paragraph 4.5.2.).

P_{is} = peak height of the internal standard, o-terphenyl,
in the trap, as measured by ultraviolet spectroscopy (paragraph 4.5.9.).

S_{is} = ultraviolet slope factor of the internal standard
(paragraphs 4.4.3. and 5.1.).

R_{uv} = recovery factor of the internal standard in the
sample, obtained by ultraviolet determination.

5.4. Internal Standard Recovery Factor-when interference in the UV is present, (by gas chromatographic area measurements). If interference is noted in the ultraviolet peak measurement of the internal standard, o-terphenyl, such as usually occurs with the high volume filters, use the integrator count of the internal standard, o-terphenyl or bibenzyl, having the lowest count for determining the recovery factor. (Because the flame ionization detector's response to the two internal standards were similar, the lowest integrator count indicates the least gas chromatographic interference.)

$$\frac{\text{o-terphenyl}}{\frac{A \times O \times 3.3}{D}} = R_{\text{Int-O}}$$

where $A = \mu\text{g}$ of o-terphenyl added to the extract (paragraph 4.5.7.2.).

O = integrator slope factor for o-terphenyl (paragraph 5.2.).

D = integrator count of o-terphenyl in the sample (paragraph 4.5.7.3.).

$R_{\text{Int-O}}$ = recovery factor of the internal standard, o-terphenyl,
using area integrator measurements.

3.3 = constant for normalizing the recovery factor to 3.0 ml
and for considering the gas chromatographic splitter
ratio - 10 to 1.

$$\text{or bibenzyl} \quad \frac{A \times B \times 3.3}{E} = R_{\text{Int-B}}$$

where $A = \mu\text{g}$ of o-terphenyl added to the extract, (paragraph 4.5.7.2.).

B = integrator slope factor for bibenzyl, (paragraph 5.2.).

E = integrator count of bibenzyl in the sample (paragraph 4.5.7.3.).

$R_{\text{Int-B}}$ = recovery factor of the internal standard, bibenzyl, using area integrator measurements.

3.3 = constant for normalizing the recovery factor to 3.0 ml and for considering the gas chromatographic splitter ratio - 10 to 1.

5.5. Weight of Polynuclear Aromatic Compounds in Membrane Filter

$$R \times P_a \times S_a \times T \times 3^n = Z_a$$

R = recovery factor for the internal standard, o-terphenyl, either R_{uv} (paragraph 5.1.), or $R_{\text{Int-O}}$, or $R_{\text{Int-B}}$ (paragraph 5.2.). The analyst must make the choice which recovery factor will give the best analytical results.

P_a = peak height for the polynuclear compound, a, in the trap as measured by ultraviolet spectroscopy (paragraph 4.5.9.).

S_a = ultraviolet slope factor for the polynuclear compound, a, in the trap (paragraphs 4.4.3. and 5.1.).

T = sampling factor. If the sample is divided and used for other types of analysis, use the appropriate factor. If the entire sample is used for gas chromatographic analysis, the sampling factor is one.

n = number of one to three dilutions made in the ultraviolet cell for the "a" polynuclear compound (paragraph 4.5.10.).

Z_a = weight of the "a" polynuclear compound in the entire membrane filter, μg .

Repeat the above calculation for the other 13 polynuclear compounds present in the remaining eight traps.

5.6. Computer Calculation of Results - A FORTRAN computer program which can be used to make the calculations and the data input card format are given in the Appendix. The first input card contains the Union Carbide Analytical number, the Government number, the integrator count (D) for o-terphenyl in the sample, the slope factor ($O \times 3.3$) for o-terphenyl, the sampling factor (T), the μg (A) of o-terphenyl added to the sample, the integrator count (E) for bibenzyl in the sample, and the slope factor ($B \times 3.3$) for bibenzyl. The second and third cards contain the ultraviolet peak and background reading for the internal standard, o-terphenyl, and all analyzed compounds.

There are three ways to obtain the recovery factor, R, of the internal standard in the sample: either by ultraviolet measurement of o-terphenyl, by integrator measurement of o-terphenyl, or by integrator measurement of bibenzyl. Only one of the three areas on the input card for calculating the recovery factor should be used. The computer program is designed to accept any one of the three approaches. If more than one area is used, the program will use the first area encountered in the sequence: UV measurement of o-terphenyl, integrator count of o-terphenyl or integrator count of bibenzyl.

6. References

- 6.1. Parma Technical Center - Notebooks 572-1 and 572-2.
- 6.2. T.D. Searl, F.J. Cassidy, W.H. King, and R.A. Brown, Anal. Chem., 42, 954 (1970).

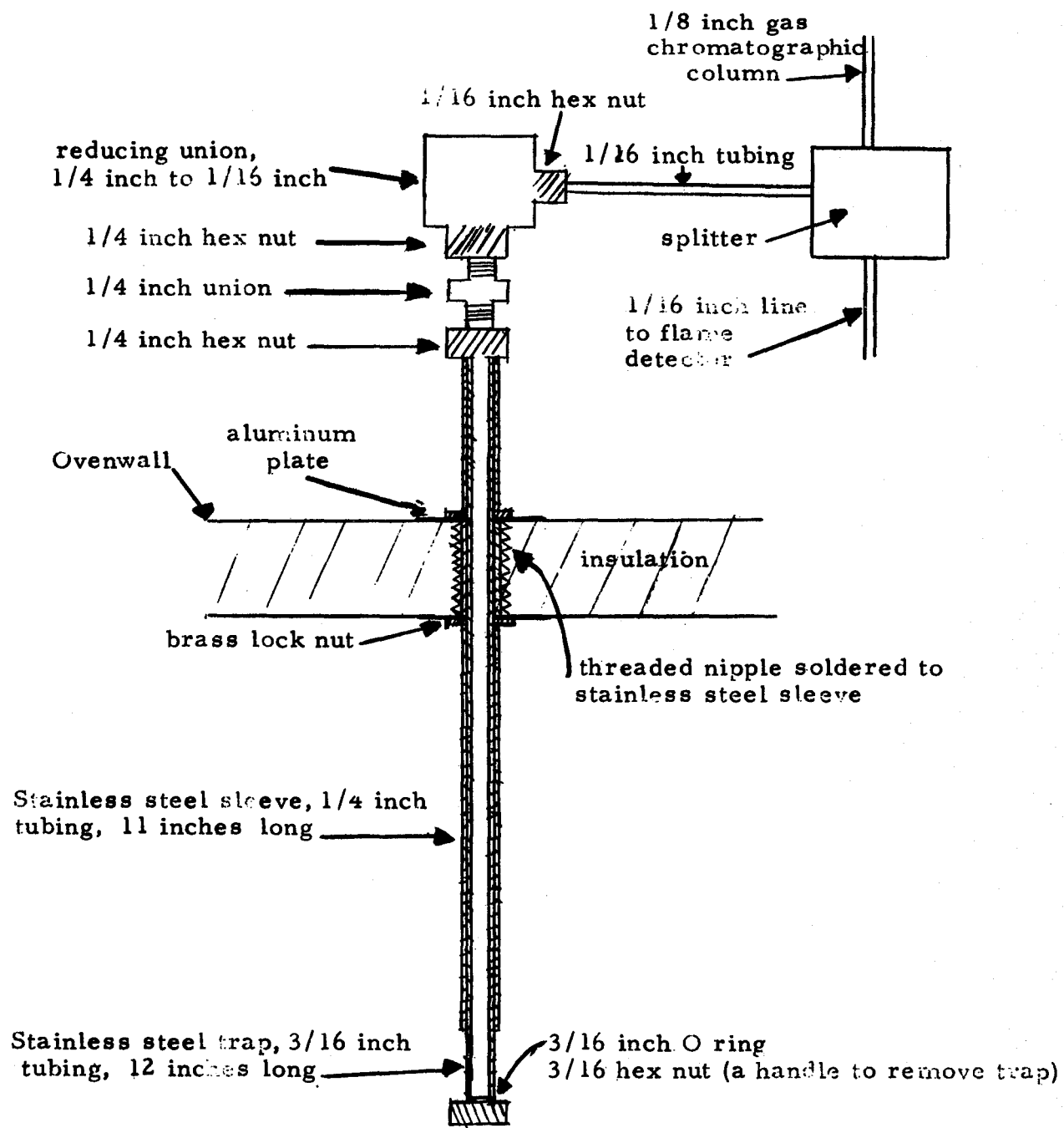


Figure 1. Gas Chromatograph Trapping Assembly.

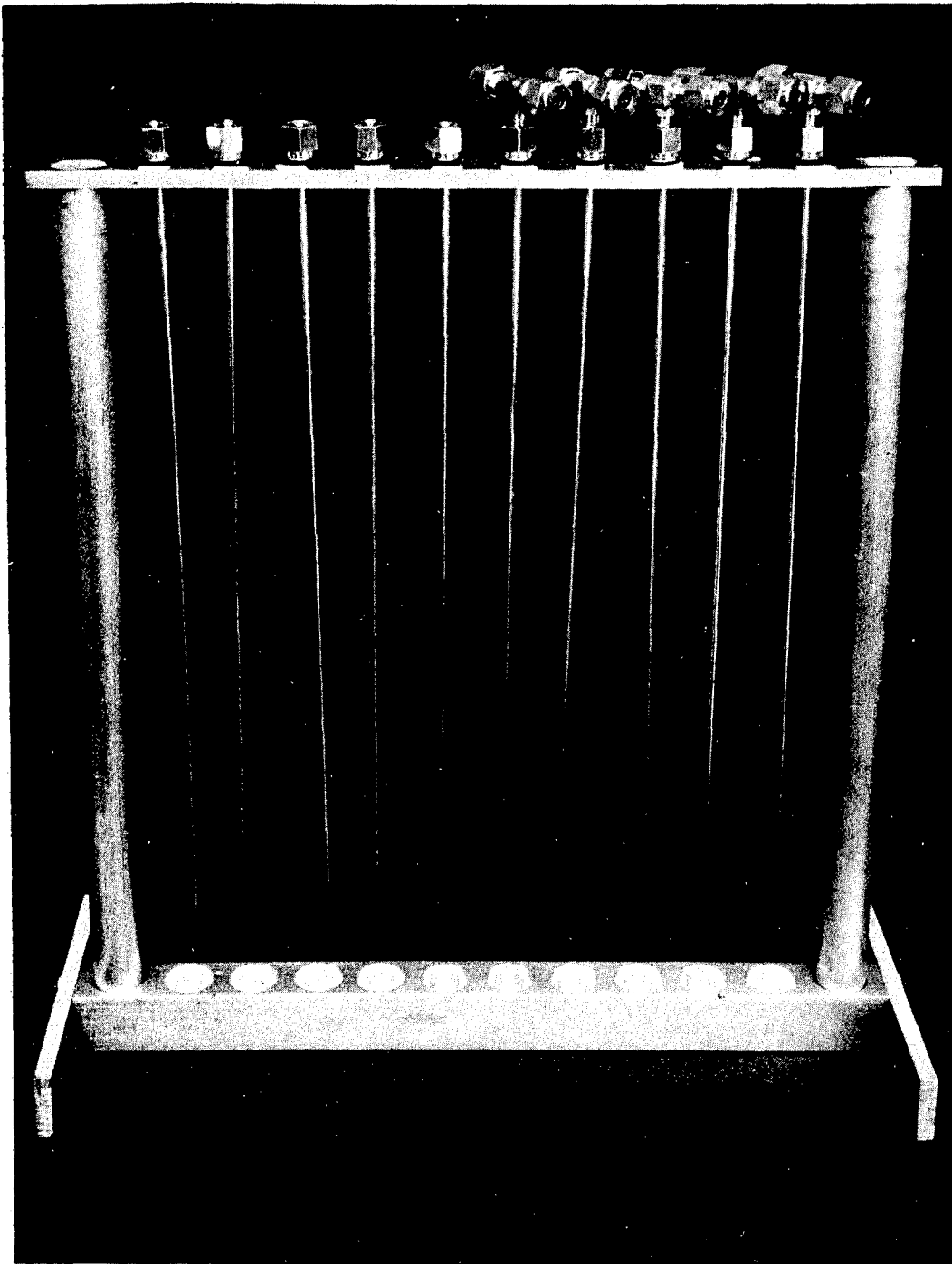


Figure 2. Trapping Rack

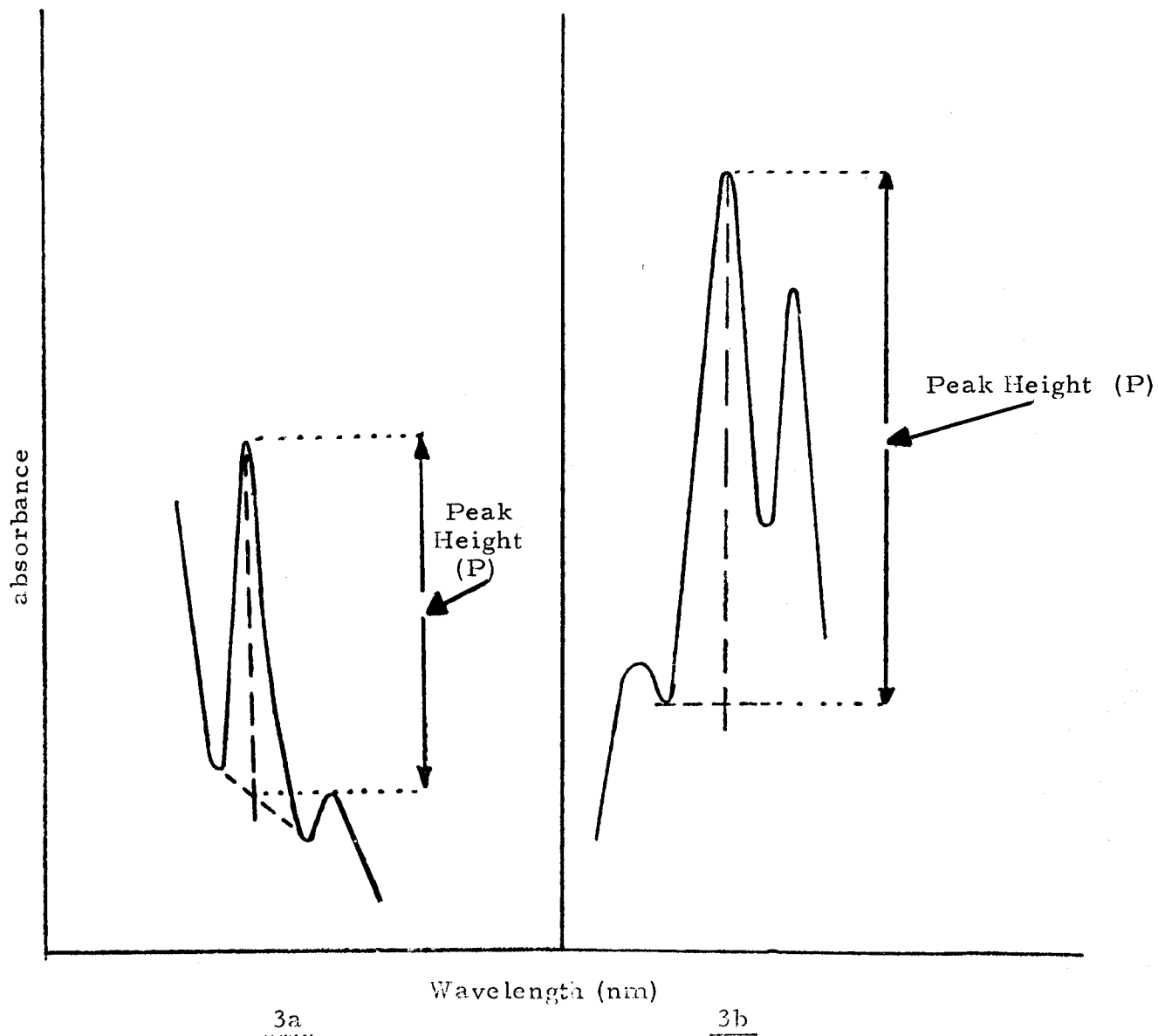


Figure 3. Measurement of Ultraviolet Peak Heights by the Sloping Baseline (3a) and the Horizontal Baseline (3b) Technique.

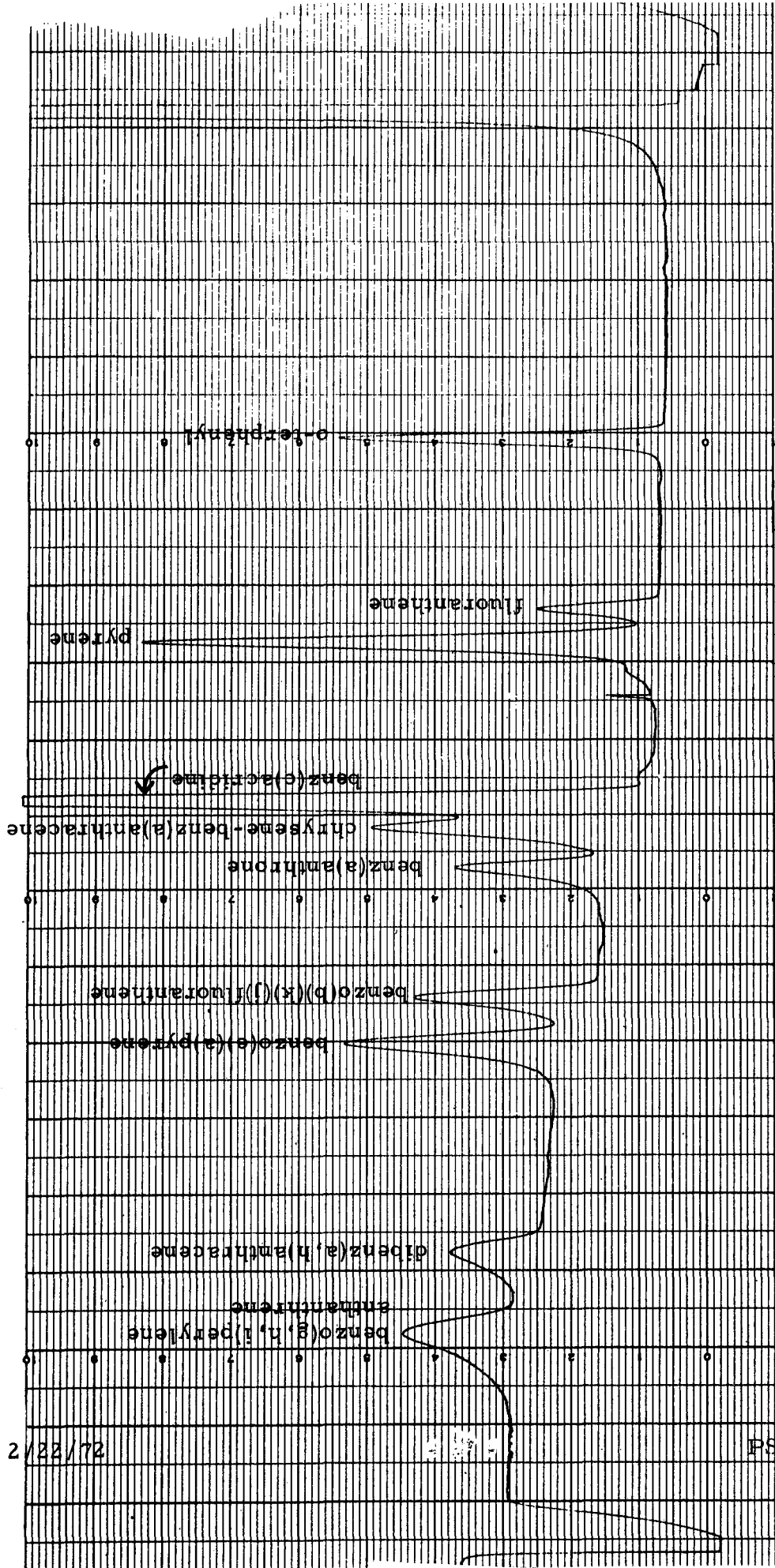


Figure 4. Chromatogram of Polynuclear Aromatic Synthetic (see paragraphs 3.3. and 4.1. for Gas Chromatographic Parameters).

A-31

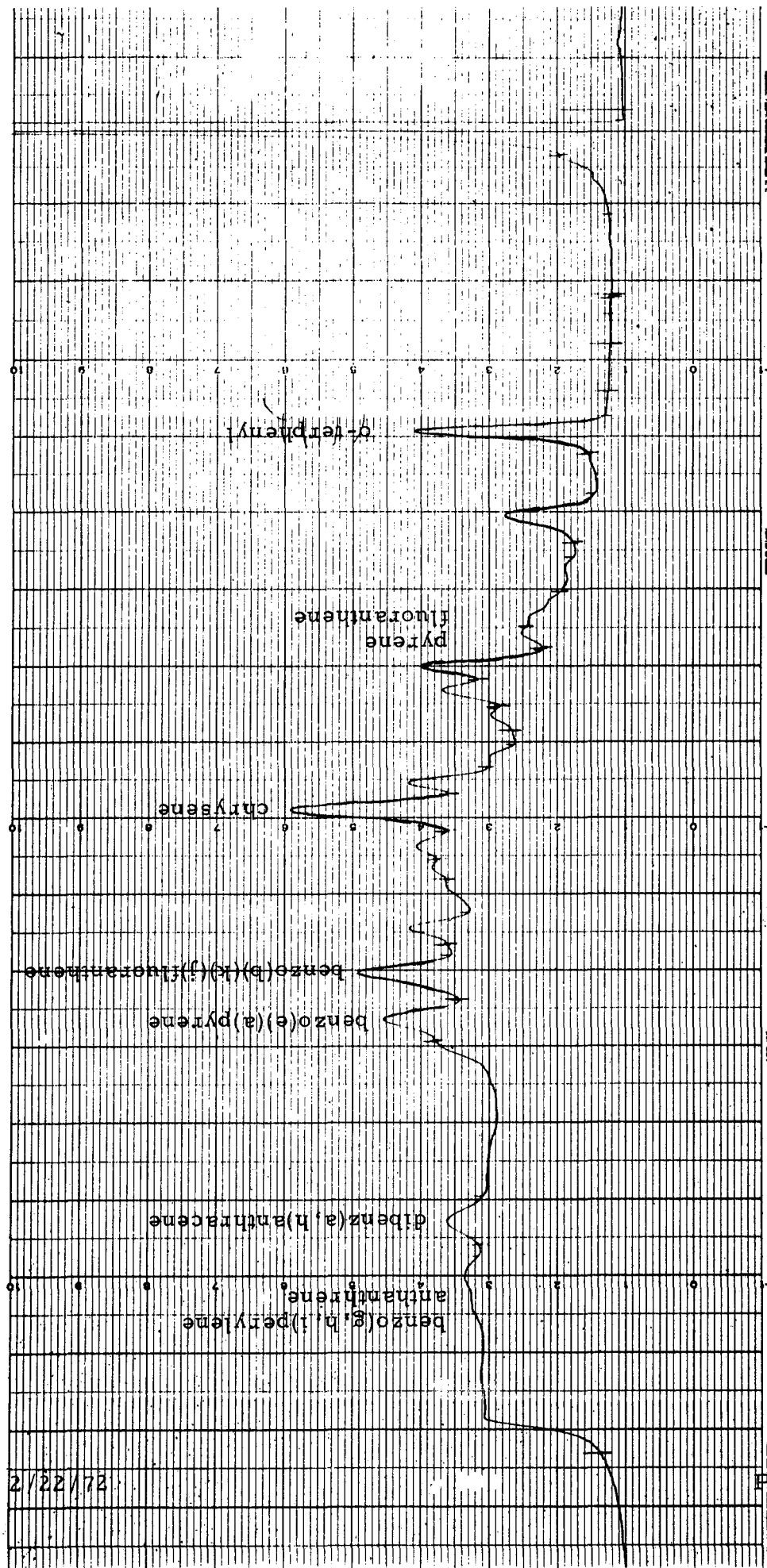


Figure 5. Chromatogram of Sample No. GS-114 (see paragraphs 3.3. and 4.1. for Gas Chromatographic Parameters).

A-32

HSM-1016

2/22/72

APPENDIX

FORTRAN Computer Program for the Calculation of Polynuclear Compounds
Trapped on Membrane Filters

```

// JOB
// FOR AL712
*IOCS(1443 PRINTER,CARD)
** GAS CHROMATOGRAPHY CALCULATIONS
*ONE WORD INTEGERS
*NUNPROCESS PROGRAM
    INTEGER ALP(8),CHECK
    REAL MICRO
    DIMENSION J(14),A1(14),A2(14),CF(14),C(14)
    DATA CF/4.8,4.0,18.0,1.88,2.51,21.0,10.5,7.8,9.6,6.4,9.1,10.2,20.0
    2,3.85/
    ICT=0
    WRITE(3,1004)
90  READ(2,1000)ALP,CTOT,SPOT,SAMF,MICRO,CTBB,SPBB,CHECK
1000 FORMAT(6X,5A2,3X,3A2,3X,F6.0,3X,F5.0,3X,F5.3,3X,F3.0,3X,F6.0,3X,F5
    1.0,6X,I1)
    IF(CHECK)100,110,100
100  CALL EXIT
110  READ(2,1001)A1OT,A2OT,(J(I),A1(I),A2(I),I=1,14)
1001 FORMAT(2F4.3,7(1X,I1,2F4.3)/7(I1,2F4.3,1X))
    IF(A1OT)120,130,120
120  F=MICRO/((A1OT-A2OT)*18.2)*SAMF
    GO TO 200
1004 FORMAT('1  AL NO      GOV NO'4X,'FLU    PYR    BCA    CHR    BAA
    1BAAN    BBF    BJF    BKF    BEP    BAP    DBAHAC BGHIP    ANT'//)
130  IF(CTOT)150,140,150
150  IF(SPOT)160,140,160
160  F=((MICRO*SPOT)/CTOT)*SAMF
    GO TO 200
140  IF(CTBB)180,170,180
180  IF(SPBB)190,170,190
170  WRITE(3,1002)ALP
1002 FORMAT(1X,'ERROR IN INTERNAL STANDARD FOR SAMPLE NO. ',5A2,2X,3A2)
    GO TO 90
190  F=((MICRO*SPBB)/CTBB)*SAMF
200  DO 210 I=1,14
210  C(I)=CF(I)*(A1(I)-A2(I))*F*3**J(I)
    WRITE(3,1003)ALP,C
1003 FORMAT(1X,5A2,2X,3A2,2X,14F7.1/)
    ICT=ICT+1
    IF(ICT-25)90,90,220
220  ICT=0
    WRITE(3,1004)
    GO TO 90
    END
// XEQ AL712
*CCEND

```

UNION CARBIDE CORPORATION
Input Card

Input Card

CHECKED BY

CODED BY

CHARGE NUMBER

DATE _____

PAGE OF

CODED BY		CHECKED BY		CHARGE NUMBER		DATE		PAGE OF	
R									
		DATA		SHEETS					
1	09	1617	2425	3233	4041	4849	5657	6465	7273
UCP 23 No.		Gov's No.		Q-TRAP SLAB CAUSE		Q-TRAP SLAB CAUSE		B-BANGS SLAB CAUSE	
235	249	336	327-345	384	380-392	267	264-275	378	420
TRAP 1	TRAP 2	TRAP 3	TRAP 3	TRAP 4	TRAP 4	TRAP 5	TRAP 5	TRAP 6	TRAP 7
B, F		B, F		B, F		B, F		B, F	
4332	524-537	332	325-338	384	398	2121	218-228	450	442
TRAP 7	TRAP 7	TRAP 8	TRAP 8	TRAP 8	TRAP 8	TRAP 9	TRAP 10	TRAP 10	TRAP 10

PARMA STANDARD TEST METHODS
UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM- 1017	ANALYSIS BaP Benzo(a)pyrene
RANGE 10 to 300 nanograms	KEY REAGENT Sulfuric Acid
PRECISION Not Determined Estimated at $\pm 10\%$ at the 200 ng level	MATRIX Membrane Filters
DATE ISSUED 2/18/72	DATE REVISED 3/24/72 e 700001

**FLUOROMETRIC DETERMINATION OF BENZO(a)PYRENE
IN AIRBORNE PARTICULATES AFTER THIN
LAYER CHROMATOGRAPHIC SEPARATION**

(This procedure utilizes PSM-1013 and PSM-1014)

1. Purpose and Limitations

1.1. This method is designed for the determination of benzo(a)pyrene (BaP) in airborne particulates which have been retained on membrane filters. It has not been evaluated as a procedure for BaP in other types of samples. Seven analyses may be completed in one work day, after the Soxhlet extractions have been made.

1.2. The blank carried through the procedure is approximately 5 ng, which is the lower limit of determination. Fluorometric response is linear for the range 10 to 300 ng, and the amount of sample must be adjusted to this range. The method is highly selective for BaP, but is sensitive to technique. Details of the procedure must be closely followed to maintain precision.

1.3. Various factors, such as nonuniformly coated plates, spotting technique, tailing effects, transfer of the developed spot, and oxygen-quenching of fluorescence, will affect the recovery of BaP. Therefore, known standards are included with each batch of chromatographic separations to locate the BaP area and to calculate a daily calibration factor.

1.4. **WARNING:** Benzo(a)pyrene and other aromatic hydrocarbons commonly found in samples containing benzo(a)pyrene are known carcinogens. Avoid skin contact with these compounds as well as the nonaqueous solvents employed in this method. Perform the

evaporations in a hood and work in a well-ventilated area to prevent contamination of the laboratory air. Forbid any flame or smoking in the laboratory when solvents such as ether are in use. Fumes from burning organic material such as pitch and coke may cause high or erratic blanks.

2. Principle of Method

2.1. Benzo(a)pyrene, together with other aromatic hydrocarbons, is extracted from the membrane filter in a Soxhlet apparatus using benzene or cyclohexane. After evaporation of the filtrate to a known volume, the components of an aliquot are separated by thin layer chromatography (TLC). Aliquots of pure BaP are located on each plate as reference standards.

2.2. The area of the TLC plate containing the BaP for each aliquot is transferred to fritted funnels, extracted with diethyl ether, and the ether is evaporated to dryness in a small beaker. The residue is dissolved in H_2SO_4 and BaP content is measured fluorometrically at 470 nm excitation and 540 nm emission wavelengths. The pure BaP standards are used for calculation of the daily calibration factor.

3. Apparatus and Reagents

3.1. Apparatus

3.1.1. Spectrophotofluorometer - American Instrument Co. model SPF, or equivalent, equipped with matched 10 mm square, fluorescence cells.

3.1.2. Thin Layer Chromatographic Apparatus - Available from Brinkmann Instruments, Inc. Equivalent apparatus may be substituted. Catalogue numbers listed below are Brinkmann's.

3.1.2.1. Coated Glass Plates - Cat. No. ALOX-25-22, 20 x 20 cm, coated with 0.25 mm thickness alumina. Place 10 plates in the rack, dry in the oven at 100°C for 30 min., and cool to room temperature. Store the rack containing the dried plates in the humidity chamber overnight. Repeat the treatment if the plates are not used within 10 days.

3.1.2.2. Drying Rack - Cat. No. 0410100-6, for 20 x 20 cm plates.

3.1.2.3. Drying Oven - Cat. No. 6010010-1.

3.1.2.4. Marking Template - Cat. No. 2509200-7, horizontally graduated at 2 cm intervals.

- 3.1.2.5. Humidity Chamber - Cat. No. 0411500-7, conditioned at 45% moisture (25°C), for receiving the drying rack. Below the shelf, place a flat dish containing 100 ml of a saturated solution of $K_2CO_3 \cdot 2H_2O$.
- 3.1.2.6. Developing Tank - Cat. No. 2510250-9, for 20 x 20 cm plates. Place a 20 x 20 cm sheet of stiff filter paper inside the tank, standing against the back wall.
- 3.1.2.7. UV Viewing Cabinet - Cat. No. 0411100-1, capable of locating the blue fluorescence of a developed spot of at least 50 ng of BaP.
- 3.1.3. Electric Hot Plate - About one sq. ft., fast response, with stepless control from 20° to 100°C, such as Fisher Scientific, Cat. No. 11-495-20. If necessary, use asbestos sheet to attain desired heat for the boiling range of various solvents used in the procedure.
- 3.1.4. Analytical Balance - Single pan type, 0.05 mg sensitivity.
- 3.1.5. Extraction Funnels - Nine required. Refer to Figure 1 for details of construction. Obtain nine 50-mm dia. funnels and nine 10 mm coarse frits, pre-sealed in 10 mm ID tubing, from a supplier such as Fisher Scientific Co. This type of funnel is more efficient than the conventional glass wool plug. Support the funnels on an adjustable rack.
- 3.1.6. All Glass Washing Bottles - Two required. Modify the item listed as Fisher Cat. No. 3-406A (500 ml) according to Figure 2. Instead of using mouth or bulb pressure to operate the washing bottle, connect a convenient length of rubber tubing from the inlet tube to a low pressure (1/4 to 1/2 lbs) nitrogen line and close the hole in the inlet tube with a finger tip.
- 3.1.7. Glassware - Twelve or more 100-ml volumetric flasks; 24 or more 30-ml beakers; two each of 2, 5, 10, 25, and 30 ml transfer pipets; one each of 5, 50, 100, and 200- μ l lambda pipets; twelve each of 5 and 10- μ l Lang-Levy pipets (Fisher Cat. No. 21-157-18); one each of 2 and 5-ml Mohr pipets, graduated in 0.1 ml divisions; 24 or more of 1-pint, wide-mouth bottles, fitted with aluminum foil in the screw cap; one 50-mm dia., short stem funnel; one 1000-ml screw cap reagent bottle; one each of 100 and 500-ml graduates; one 500-ml glass stoppered bottle.

3.1.8. Miscellaneous - Two 500-ml plastic washing bottles; dissecting knife; camel's hair brush; refrigerator (for routine storage of Soxhlet extracts, if necessary); small rubber bulb for micropipets; lint-free tissues; cylinder of compressed nitrogen with pressure reducing valves; aluminum foil.

3.2. Reagents

3.2.1. Benzene, Pentane, and Cyclohexane - Spectranalyzed grade, available from Fisher Scientific Co.

3.2.2. Diethyl Ether and Methanol - ACS reagent grade.

3.2.2.1. Pentane-Ether Mixture (18:2) - Add 720 ml of pentane to a one liter screw cap bottle, add 80 ml of diethyl ether, cover the bottle opening with aluminum foil, and cap tightly. Mix gently and store in a cool place. Just before marking the TLC plates (paragraph 4.2.3.), pour sufficient pentane-ether mixture into the developing tank to form a pool 1 cm deep. Empty the tank and discard the mixture after each day of use.

3.2.3. Sulfuric Acid - ACS reagent grade, free from extraneous oxidants. To 300 ml of H_2SO_4 in the glass stopper bottle add 0.5 g of hydrazine sulfate. Purge for 30 min. with nitrogen. Repeat the purge for 15 min. just before use. Avoid unnecessary exposure to room air as a means of retarding the moisture absorption.

3.2.4. Nitric Acid - For cleaning glassware.

3.2.5. Benzo(a)pyrene (BaP) - 99% or greater purity. Purify unknown quality reagent by column chromatography as described in PSM-1018.

3.2.5.1. Standard BaP Solution - Weigh a 30-ml beaker, add about 20 mg of BaP, and reweigh to the nearest 0.05 mg. Obtain the weight of BaP by difference. To the beaker add 20 ml of benzene, dissolve and transfer to a 100-ml volumetric flask using the glass washing bottle (Apparatus 3.1.6.) containing benzene. Dilute to the mark with benzene and mix. Each ml contains about 0.2 mg of BaP (viz. $\frac{\text{mg of BaP}}{100}$), or each μl (microliter) contains about 0.2 μg (microgram) of BaP. With a pipet transfer 10 ml of this solution to another 100-ml volumetric flask. Dilute to the mark with benzene and mix. Each μl of the diluted solution contains about 20 ng (nanogram) of BaP. Store the solutions in a dark place.

4. Procedure

4.1. Preliminary Considerations

4.1.1. Clean all glassware with warm HNO_3 . Rinse several times with distilled water and finally with methanol to remove water. Once initially cleaned, pipets may be rinsed with benzene from the washing bottle immediately after use. Rinse pipets finally with methanol and dry in an upright position, or blow dry with a bulb.

4.1.2. Reserve a complete set of glassware to be used only for this determination. Work on a scrupulously clean surface in a laboratory that is free from dust, smoke, and oxidizing acid fumes.

4.1.3. One should become familiar with the TLC technique by practice with the standard BaP solution before attempting the analysis of samples. This practice will also demonstrate the linearity of fluorescence intensity with increasing BaP concentration for the range 10 to 300 ng.

4.1.4. Using benzene or cyclohexane, according to the nature of the membrane filters containing the samples, prepare Soxhlet extractions as described in PSM-1013 or 1014. If only a portion of the membrane filter and/or the Soxhlet solution (before evaporation) is intended for this determination, record this decimal portion of the entire filter as "H" for subsequent calculations. Caution: before extracting low level samples, make certain that the apparatus has been thoroughly cleaned. It is convenient to make TLC separations with a batch of six samples per day. Store the surplus extractions in a refrigerator at 4°C.

4.1.5. Place the pint-bottles containing the six extractions on a hot plate set at 80°-90°C. Adjust the temperature to near the boiling range of the solvent. Evaporate to about 50 ml. If the solutions are colorless, proceed to paragraph 4.4. If the solutions are colored yellow to brown, set them aside and cool to room temperature. Experience has shown that the colored solutions usually contain large amounts of benzo(a)pyrene.

4.2. Procedure for Range Greater than 0.1 µg BaP (high level)

4.2.1. Transfer the colored solutions to numbered 100-ml volumetric flasks via a small funnel. Rinse the bottle 3 or 4 times by means of the all glass washing bottle (Apparatus 3.1.6.) containing the extraction solvent. Add the rinses to the flask, wash down the funnel, dilute to the mark, and mix.

4.2.2. Transfer an aliquot (1 to 30 ml) by means of pipets from each flask to numbered 30-ml beakers. Select an aliquot volume that will limit the BaP to about 0.2 μg after the TLC separation. (Note that an additional dilution occurs in paragraph 4.2.5..) The precise amount of aliquot can be judged only by experience.

4.2.3. Evaporate the aliquots on a hot plate set near the boiling range of the solvent (80°-90°C). When the volume is about 0.3 ml remove the beakers and let the remaining solvent evaporate during the cooling period. Do not evaporate to dryness on the hot plate. While the beakers are cooling, mark a prepared TLC plate (Apparatus 3.1.2.1.) by means of the marking template, with a pencil dot at 2 cm intervals and 1.5 cm above the bottom edge of the plate. Nine spots should be located on the 20 x 20 cm plate. Reserve position No. 1 on the plate for the daily method blank.

4.2.4. With a small rubber bulb, fill a 10- μl Lang-Levy pipet with diluted BaP standard (Reagent 3.2.5.1. twenty ng/ μl) to a level above the constriction, which is the index. Adjust the level to the index by gentle contact with a lint-free tissue. Transfer the aliquot to spot No. 2 on the TLC plate (left side) by repeated, very short interval contact between the pipet tip and the plate. Control the diameter of the wetted spot to 5 mm and avoid chipping the alumina coating. Repeat this step for spot No. 9 (right side).

4.2.5. To the first cool beaker of the batch of six (paragraph 4.2.3.), add 200 μl of benzene by means of a lambda pipet. Apply a gentle rotary motion to the beaker to aid in dissolution of the residue. Within 45 seconds fill another 10- μl Lang-Levy pipet with the sample solution and transfer to spot No. 3 on the plate, using the technique described in paragraph 4.2.4. For each of the remaining five samples, repeat this step in sequence. Save the samples in the beakers. Complete the loading of the plate by applying, as a method blank to spot No. 1, 10 μl of the Soxhlet extraction solvent currently in use.

4.2.6. With located spots positioned near the lower edge, place the plate vertically in the developing tank containing pentane-ether mixture (Reagent 3.2.2.1.). Prevent bright light from hitting the plate by covering the closed tank with a towel or paper box. When

the solvent front has migrated to about 3 cm below the top edge (about 20 minutes) remove the developed plate and place under the UV viewer. Orient the plate horizontally with original location of the spots closest to the analyst (see Figure 3).

4.2.7. Find the developed standard spots (above Nos. 2 and 9) by their blue fluorescence. The fluorescence is more discernible if room lights are off. As quickly as possible, for each standard spot, place a pencil mark about 1 mm beyond the limit of visible detection. Place another mark about 2 mm before the detected spot to compensate for tailing effect. Immediately remove the plate from the viewer.

4.2.8. With the aid of a ruler gently draw two pencil lines horizontally connecting the located marks. The space between the lines will include the BaP in the samples as well as the standards. If the width of the space is more than 1.5 cm or if the standards have not migrated at least 1.5 cm, the original spotting technique and/or the plate is defective. Discard the plate and use the corrective step described in paragraph 4.2.8.1.; otherwise proceed with paragraph 4.2.9..

4.2.8.1. Corrective Step - in case of unsatisfactory TLC separation
Return to the sample beakers (paragraph 4.2.5.) to which had been added 200 μ l of benzene just prior to spotting. Evaporate to dryness, if not already so, cool, and add another 200 μ l of benzene. Continue with the spotting of standards, samples, and blank as described in paragraph 4.2.3. through 4.2.8., using greater care and a freshly prepared plate. Note that this repeated separation requires a correction factor as described in the calculations.

4.2.9. Proceeding from left to right, transfer the alumina coating, which represents each migrated spot of BaP, to each of nine extraction funnels (Apparatus 3.1.5.), in sequence. Hold the edge of the plate in contact with the funnel rim and with the marked lines diametrically centered over the funnel. Tilt the plate to a flat angle (about 15°). Gently scrape loose the first spot with a dissecting knife using short abrasive strokes at a low angle of attack. Direct the strokes toward the funnel. Tilt the plate at a steeper angle and tap the opposite edge of the plate to transfer the loose material.

Restrict the scraping of each spot within the marked lines and to the midpoint between each spot. Using only the tip of a small brush, carefully transfer the fine particles. The glass substrate should be clear before proceeding to the next spot. Use the cleared channel as a glide path for each sequential transfer. After spot No. 5 has been removed, begin again at spot No. 9, over the appropriate funnel, to reduce the length of glide path.

4.2.10. Place clean 30-ml beakers marked 1 thru 9 respectively, under the funnel stems and locate the funnel rack in a well ventilated hood. Carefully wash down the fine particles on the funnel cone with diethyl ether from an all glass washing bottle (Apparatus 3.1.6.) after adjusting the nitrogen pressure for minimum emission of vapor phase. Continue adding ether in 5 ml increments to the funnels until a total of 30 ml has been collected in each beaker. Place the beakers on a hot plate set at 30°C and evaporate to about 0.3 ml. Remove the beakers and let the remaining solvent evaporate during the cooling period. Do not bake dry.

4.3. Fluorescence Measurement

4.3.1. Instrumental Parameters for the Aminco Model SPF

4.3.1.1. Follow the manufacturer's instruction for a 5 minute warm up.

4.3.1.2. Excitation wavelength - 470; emission wavelength - 540.

4.3.1.3. Entrance slit - 1 mm; exit slit - 1 mm; blank slit - open; PM slit - 1 mm.

4.3.1.4. Response switch - 3.

4.3.1.5. Chopper switch - on.

4.3.1.6. Mode switch - manual.

4.3.1.7. High voltage control - 600 V on the meter.

4.3.1.8. Recorder - off.

4.3.1.9. With shutter closed and the sensitivity switch in zero adjust position, rotate the zero adjust vernier to obtain a zero reading on the intensity meter.

4.3.1.10. Set the sensitivity switch at 0.1, the sensitivity vernier at 0, and the blank subtract switch in lo-range. Fill a 10-mm square cell with prepared H₂SO₄ (Reagent 3.2.3.) as reference solution. Place in the cell compartment and replace the compartment cover.

Open the shutter, set the mode switch at ratio, and adjust the blank subtract vernier to obtain a zero reading on the intensity meter. The instrument is ready now for fluorescence measurement of samples. Set the mode switch at manual and close the shutter for standby.

4.3.2. With a 2-ml Mohr pipet, transfer 1.5 ml of prepared sulfuric acid to beaker No. 1 containing the method blank from paragraph 4.2.10.. Carefully tilt the beaker and rotate between the fingers until the H_2SO_4 has wetted the wall to within 1 cm of the rim. Hold the beaker upright, gently swirl the contents for about 15 seconds, then pour into a clean dry 10-mm square cell.

4.3.3. Repeat the H_2SO_4 blank subtract adjustment previously established in paragraph 4.3.1.10. Replace the reference cell in the compartment with the cell containing the contents of beaker No. 1 (method blank). Open the shutter, set the mode switch at ratio, and measure the relative intensity after changing the sensitivity switch to obtain a near mid-scale reading. Record both the meter reading and the sensitivity position (viz. meter multiplier).

4.3.4. Replace the reference cell in the compartment. Discard the contents of the cell containing the method blank, rinse several times with water, and finally with methanol from a washing bottle. Dry the cell with a jet of nitrogen while holding it firmly with lint-free tissue.

4.3.5. Continue with preparation and measurement for beakers No. 2 and 9, as described in paragraphs 4.3.2. through 4.3.4. Beakers No. 2 and 9 contain the BaP standards.

4.3.6. Repeat the preparation and measurement, as described in paragraphs 4.3.2. through 4.3.4., for beakers No. 3 through 8 which contain the samples.

4.4. Procedure for Samples in the Range 0 to 0.1 μg of BaP (low level)

4.4.1. Perform Soxhlet extractions on unexposed (blank) membrane filters of the type currently in use employing benzene, cyclohexane, or other specified solvents. Determine their BaP content in the same manner as for low level samples. Designate the meter reading and meter multiplier obtained for this sample blank as Y and Z, respectively.

4.4.2. After six filtrates from the Soxhlet extractions have been concentrated to 50 ml or less (see paragraph 4.1.5.) and solutions appear to be colorless, continue with evaporations to about 10 ml. Transfer to numbered 30-ml beakers, using the all glass washing bottle containing the extraction solvent to complete the transfer. Place the beakers on the hot plate and evaporate to about 0.3 ml at temperature near the boiling range of the solvent. Remove the beakers and let the remaining solvent evaporate during the cooling period. Do not bake dry.

4.4.3. Mark a prepared TLC plate (Apparatus 3.1.2.1.) at 2 cm intervals and 1.5 cm from the bottom edge. With a Lang-Levy pipet transfer a 5- μ l aliquot of the diluted BaP standard (Reagent 3.2.5.1. -twenty ng/ μ l) to marked positions No. 2 and 9 on the plate. Use the technique described in paragraph 4.2.4. for spotting these standards and samples which follow. Reserve position No. 1 for a daily method blank which consists of 10 μ l of the Soxhlet extraction solvent currently in use.

4.4.4. To the first beaker of the batch of six containing the evaporated samples, add 50 μ l of benzene by means of a lambda pipet. Apply a gentle rotary motion to the beaker as an aid in dissolution of the residue. Within 30 seconds fill another 10- μ l Lang-Levy pipet with the sample solution and transfer to position No. 3 on the plate. Similarly, transfer an aliquot of the remaining five samples to appropriate positions on the plate.

4.4.5. Develop the plate, transfer the developed spots, extract with ether, and make fluorescence measurements as described in paragraphs 4.2.6. through 4.3.6. If the TLC separation is judged unsatisfactory, use Corrective Step 4.2.8.1. In this case use only 50 μ l of benzene instead of 200 μ l.

5. Calculations

5.1. Daily Calibration Factor

$$\frac{A}{(B \times C) - (L \times M)} = F$$

where A = ng of BaP spotted on the TLC plate
(viz. pipet vol x ng/ μ l. value of std.)
(paragraph 4.2.4., or 4.4.3. for low
level procedure)

B = intensity meter reading (avg. of 2 std. spots Nos. 2 and 9) (paragraph 4.3.5.)
 C = meter multiplier used to obtain reading for standards (paragraph 4.3.5.)
 L = meter reading for method blank, spot No. 1 (paragraph 4.3.3.)
 M = meter multiplier used to obtain reading for method blank (paragraph 4.3.3.)
 F = calibration factor as ng per intensity meter unit.

5.2. BaP Content of Samples (high level)

$$\left(\frac{200}{190}\right)^N \times \frac{2F}{G \times H} [(D \times E) - (L \times M)] = \mu\text{g of BaP in sample}$$

where D = intensity meter reading for each sample (paragraph 4.3.5. for spots 3 through 8)

E = meter multiplier used to obtain reading for each sample (paragraph 4.3.6.)

F = calibration factor (paragraph 5.1.)

G = ml of aliquot taken from volumetric flask (paragraph 4.2.2.)

H = Sampling factor (paragraph 4.1.4.). If entire sample is given to analyst, sampling factor is 1. If only a portion is given to the analyst, use appropriate weight factor less than 1.

L = } see paragraph 5.1.
 M = }

N = number of times the corrective step (paragraph 4.2.8.1.) is applied. If the corrective step is omitted, N = 0 and the quantity $\left(\frac{200}{190}\right)^N = 1$.

5.3. BaP Content of Sample Blank

$$\left(\frac{50}{40}\right)^N \times 5F [(Y \times Z) - (L \times M)] = P \text{ as ng of BaP}$$

where P = Sample blank obtained by Soxhlet extraction
of unexposed membrane filter (paragraph 4.4.1.).
Calculate P from the fluorescence intensity data
obtained by means of the low level procedure.

Y = intensity meter reading for sample blank
(paragraph 4.4.5.)

Z = meter multiplier used to obtain sample blank
reading (paragraph 4.4.5.)

F = }
L = } see paragraph 5.1.
M = }

N = see paragraphs 5.2. and 4.4.5. (If the
corrective step is omitted, N = 0 and
 $(\frac{50}{40})^N = 1.$)

5.4. BaP Content of Samples (low level)

$$\left(\frac{50}{40}\right)^N \times 5F [(J \times K) - (L \times M)] - P = \text{ng of BaP in sample}$$

where F = calibration factor (paragraph 5.1.)

J = intensity meter reading for sample
(paragraph 4.4.5.)

K = meter multiplier used to obtain sample
reading (paragraph 4.4.5.)

L = }
M = } see paragraph 5.1.

N = see paragraphs 5.2. and 4.4.5. (If the
corrective step is omitted, N = 0 and
 $(\frac{50}{40})^N = 1.$)

P = sample blank (paragraph 5.3.)

6. References

- 6.1. Health Lab. Sci., 7, 56-59 (1970).
- 6.2. Sawicki, E., et al., Anal. Chem. 36, 497 (1964).
- 6.3. Parma Technical Center, Notebook 572-3.

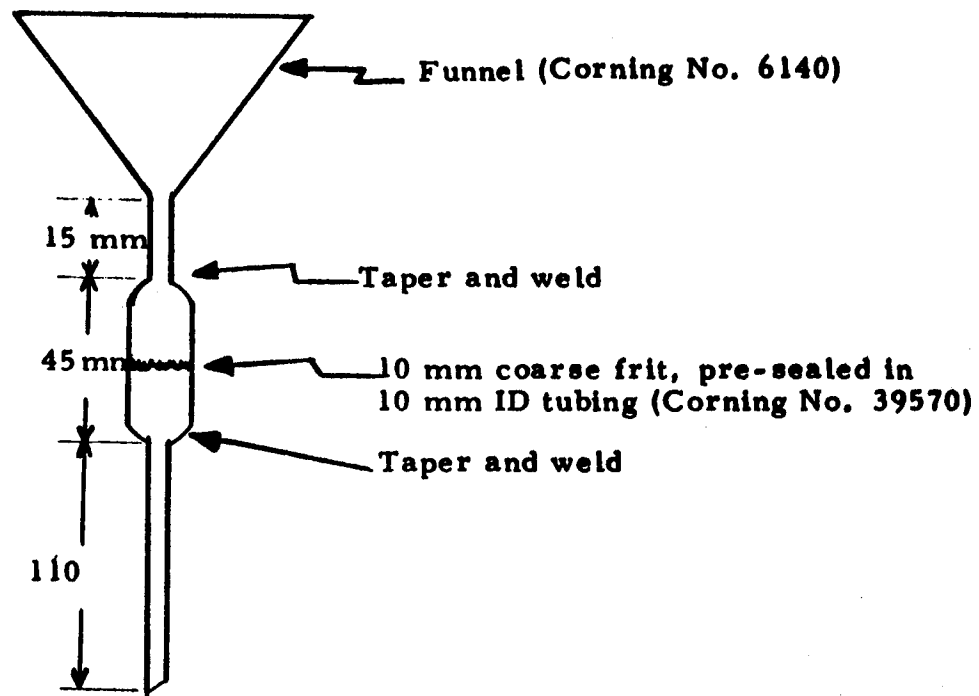


Figure 1. Extraction Funnel

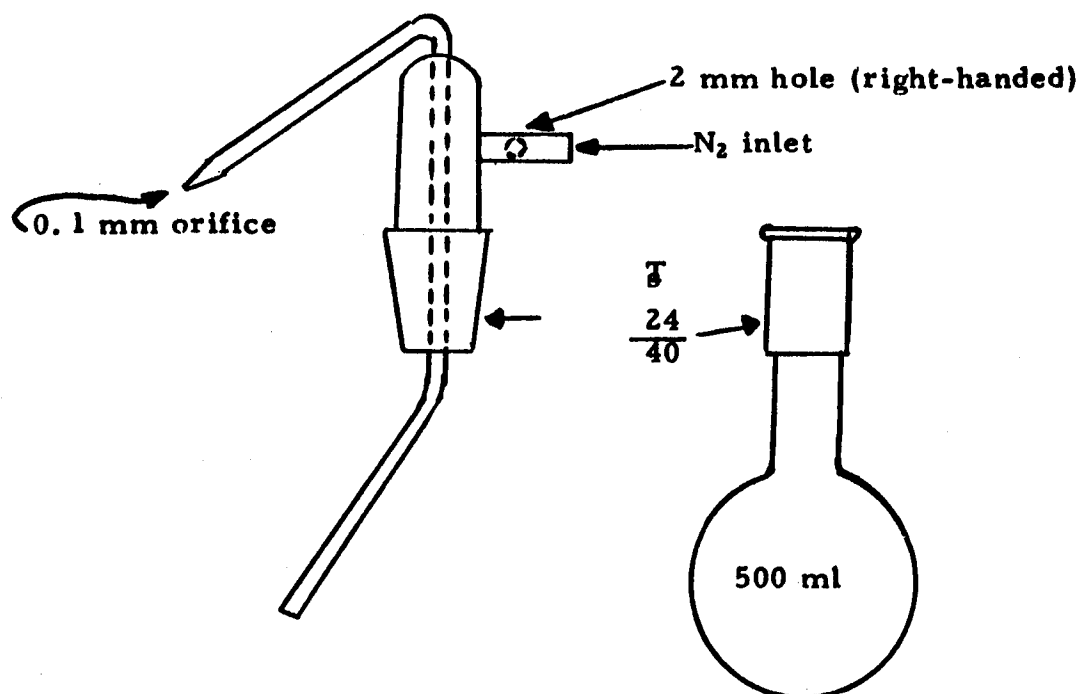


Figure 2. All Glass Washing Bottle

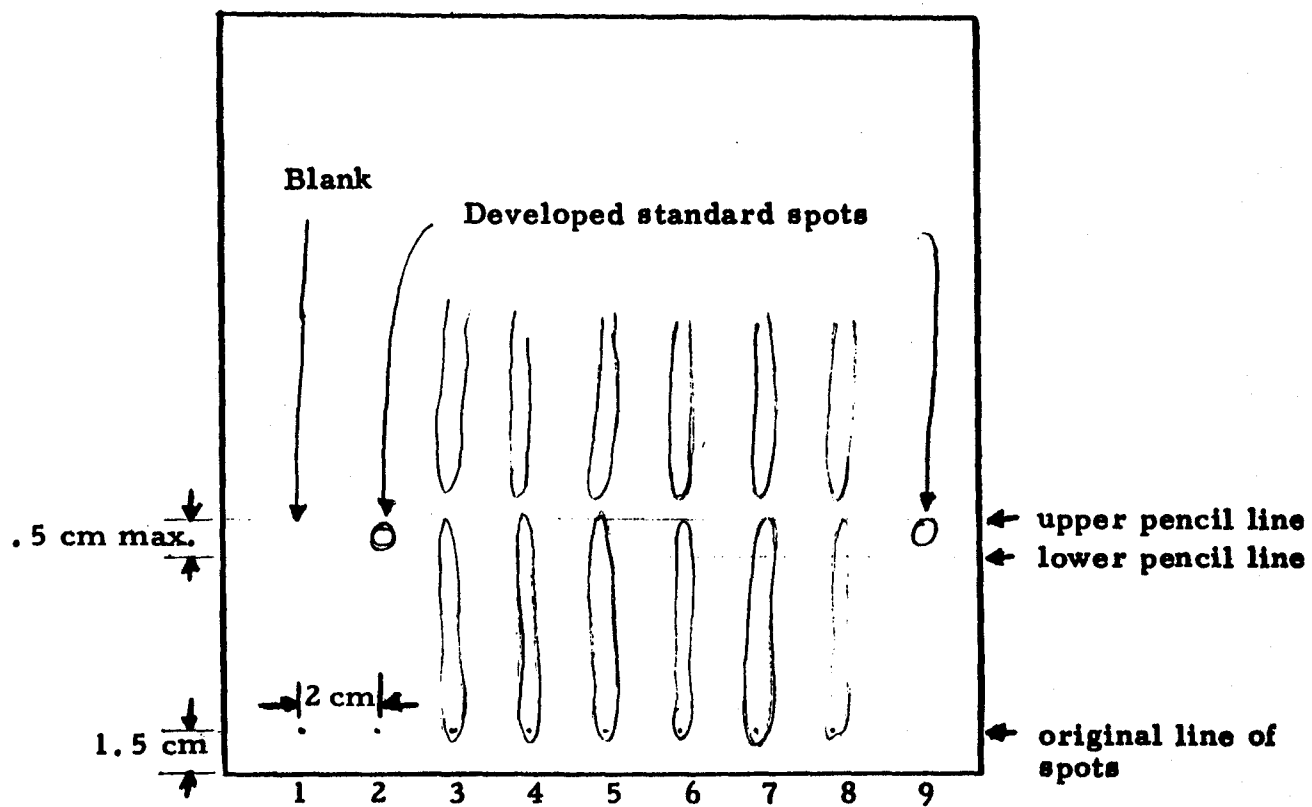


Figure 3. Developed TLC Plate

PARMA STANDARD TEST METHODS
UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM-1019	ANALYSIS Polynuclear Aromatic Compounds
RANGE 0 → 3 mg(benzene solubles) or aliquot of larger sample	INSTRUMENT Spectrophotometers Liquid Chromatography Separation
PRECISION Not determined	MATRIX Airborne Particulates Trapped on Air Sampling Filters
DATE ISSUED 6/19/72	DATE REVISED 6700142

LIQUID CHROMATOGRAPHIC SEPARATION AND
SPECTROPHOTOMETRIC DETERMINATION OF POLYNUCLEAR
AROMATIC HYDROCARBONS IN AIRBORNE PARTICULATES
AFTER SOXHLET EXTRACTION

(This method utilizes PSM-1013, 1013a, 1018)

1. Purpose and Limitations

1.1. This method is suitable for the determination of pyrene, fluoranthene, benz(a)anthracene, chrysene, benzo(e)pyrene, benzo(a)pyrene, perylene, benzo(k)fluoranthene, and anthanthrene in the benzene extract from airborne particulates collected on various filter media.

1.2. The separation and quantification of these nine hydrocarbons is quite dependent and interdependent on the following factors: moisture level of the alumina, reproducibility of the packing of the columns, humidity level in the laboratory, moisture level of the solvents, resolving power of the absorption spectrophotometer, selectivity of H₂SO₄ solutions for fluorometric determination of benzo(a)pyrene, interference from other unknown components contained in the fractions, quality of reference hydrocarbons, correction of the absorbance values for interfering compounds, and quantity of sample separated.

1.3. This analysis requires considerable "art" as well as manipulatory skills and a high degree of consistency for satisfactory results.

1.4. Many of the polynuclear aromatic hydrocarbons commonly found in air pollution particulates are known carcinogens. Avoid skin contact with these particulates and with any solution containing these compounds. Perform the solvent mixing and the column chromatographing in a well-ventilated area.

. Principle of the Method

. 1. The benzene soluble components collected on a filter are extract

in a Soxhlet extraction apparatus (PSM-1013, 1013a). Hydrocarbons of interest from all or an aliquot of this extract are separated by use of an alumina-packed column and n-pentane-ether mixtures as the elution solvents.

2.2. The fractions collected are scanned by absorption spectroscopy and specific fractions are examined by fluorometry. The absorption spectra are used to determine the absorbances at designated wavelengths for specific compounds. The fluorometer is used to determine the amount of benzo(a)pyrene. Because of mutual interferences a computer program is used to calculate the concentrations of the nine polynuclear hydrocarbons.

3. Apparatus and Reagents

3.1. Apparatus

3.1.1. Recording spectrophotometer - Varian Associates, Cary Model 14 or equivalent.

3.1.2. Absorption cells - matched 10-mm pathlength cells, Suprasil, available from Fisher Scientific, Cat. No. 14-385-904C or equivalent. Calibrate these cells, except for one reference cell, with distilled water by weighing 1.00 and 3.00 g of water and marking the meniscus level on the cells.

3.1.3. Absorbance screens - neutral density screens of three absorbance values available from Varian Associates, Cary Part No. 1404109 or equivalent.

3.1.4. Ratio spectrophotofluorometer - American Instrument Co., Model SP-F or equivalent equipped with square 10-mm pathlength cells, available from Fisher Scientific, Cat. No. 14-385-920A or equivalent.

3.1.5. Glassware - assorted 25, 10, 5, and 1-ml pipets; assorted 25, 50, and 100-ml volumetric flasks; 1000-ml graduated cylinder; seven 1-gal jug-form bottles with caps; four 1-l beakers; nine 30-ml beakers; one Buchner funnel, 18.5-cm diameter fitted with a No. 9 rubber stopper; one 2-l filtering flask; one 10-ml graduated cylinder TD; glass stirring rods; an assorted number of 1-qt wide-mouth bottles; one reagent bottle; and for each sample: one 150-ml graduated beaker, one 60° long stem funnel, fifty 2-oz bottles, twenty 5 3/4" Pasteur pipets and one 9" Pasteur pipet (available from Fisher Scientific, Cat. No. 13-678-5A and 5B, respectively).

3.1.6. Columns - assemble according to Figure 1.

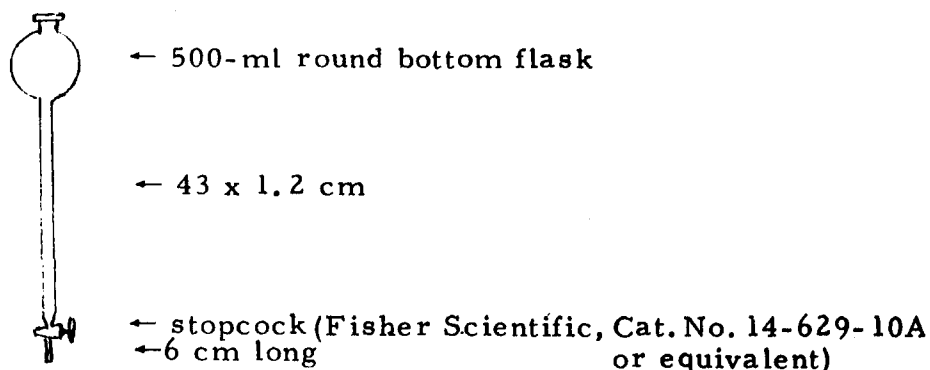


Figure 1.

3.1.7. Freezer - available from Fisher Scientific, Cat. No. 13-988-30 or equivalent.

3.1.8. Oven - available from Fisher Scientific, Cat. No. 13-244-1 or equivalent.

3.1.9. Analytical Balance - single pan type, 0.05 mg sensitivity.

3.1.10. Triple beam balance - single pan type.

3.1.11. Cuvette Washer - Available from Chemical Rubber Company, Cat. No. 2735-304 or equivalent.

3.1.12. Ultraviolet lamp, long wavelength (3660A) available from Fisher Scientific, Cat. No. 11-984-1 or equivalent.

3.1.13. Miscellaneous - Pipet filler, Fisher Scientific, Cat. No. 13-681-50 or equivalent; assorted spatulas; Pyrex glasswool (washed with chloroform and dried); buret brush; 8-inch forceps; 10 trays, 23 x 33 cm (for storage); aluminum foil; bottle brush; Plexiglass rod, 1-cm diameter and ~70-cm length; atomizer rubber bulb attached by rubber tubing to glass rod in a No. 6 rubber stopper; steel rod ~3-mm diameter and 70-cm. length; plastic washing bottles; filter paper, 18.5-cm diameter; rubber bulbs, 1-ml and 2-ml volume; vacuum tubing.

3.1.14. Cell Rack - for 1-cm cells, available from Wilkens-Anderson Company, or equivalent.

3.2. Reagents

3.2.1. Chloroform and n-Pentane - spectranalyzed, available from Fisher Scientific, or equivalent.

3.2.2. Diethyl ether - anhydrous, available from Fisher Scientific, or equivalent.

3.2.3. Chloroform - laboratory grade, available from Fisher Scientific, or equivalent.

3.2.4. Methanol, acetone, sulfuric acid, and hydrochloric acid - ACS certified grade, available from Fisher Scientific, or equivalent. Prepare dilute HCl by adding ~10 ml of acid to ~1l of distilled water.

3.2.5. Silica gel - 28-200 mesh, grade 12 available from Fisher Scientific, or equivalent. Slurry 200-500 g four times with anhydrous ether (reagent 3.2.2.). Place the filter paper in the Buchner funnel, place the funnel on the filtering flask, and attach the side arm to an aspirator. Add sufficient ether to seat the paper. Filter the slurry through the Buchner funnel. Air dry the silica gel overnight in the hood. Dry for 2 hours at 130°C in the oven (apparatus 3.1.8.) after no ether odor remains. Store in a tightly capped bottle.

3.2.6. Polynuclear Aromatic Hydrocarbon Standards (PNA) - pyrene, fluoranthene, benzo(a)anthracene, chrysene, benzo(e)pyrene, benzo(a)pyrene, perylene, benzo(k)fluoranthene, anthanthrene. The suppliers of these compounds are scarce and synthesis may be required. Purify the aromatic hydrocarbons by column chromatography as described in PSM-1018.

3.2.7. Alumina - acid washed, 100-200 mesh from Merck and Co., Cat. No. 71695 available from C.P. Hall Co., Stow, Ohio, (see limitations in paragraph 1.2.), or any alumina that yields satisfactory separations.

3.2.8. Elution mixtures - prepare and store in tightly capped 1-gal jug-form bottles mixtures of diethyl ether and n-pentane. Transfer 970 ml of n-pentane into the 1000-ml graduated cylinder, add 30 ml of ether, and pour into a 1-gal jug. Repeat one or two more times to fill the jug. Label this mixture 3%. Prepare additional mixtures in like fashion by using the volumes in Table I. Label as indicated in Table I.

TABLE I		
Volume (ml)		Label
<u>n-pentane</u>	<u>ether</u>	
940	60	6%
910	90	9%
880	120	12%
850	150	15%
820	180	18%
750	250	25%

4. Procedure

4.1. Glassware cleaning - Initially clean all glassware by separately

rinsing once with dilute hydrochloric acid, distilled water, methanol, and n-pentane. Check all glassware with the UV lamp in the dark to verify that no fluorescent materials remain. After this initial cleaning, for all subsequent cleaning rinse with chloroform (2 times), methanol, and n-pentane. (Rinsing of bottles can more easily be done by dipping bottles held by forceps into solvents in 1-ℓ beakers.)

4.2. PNA calibration solutions

4.2.1. Separate standards - Weigh exactly 10 mg of each PNA (reagent 3.2.6.) into a 30-ml beaker. Transfer quantitatively into a 100-ml volumetric flask with n-pentane. Dilute to volume with n-pentane (concentration 100 µg/ml). Transfer, with pipette, exactly 1 ml to a second 100-ml volumetric flask, a 50-ml volumetric flask, and a 25-ml volumetric flask, and 5 ml to a 50-ml volumetric flask and dilute all to volume with n-pentane. These four solutions contain 1, 2, 4, and 10 µg/ml, respectively. Cover these flasks with aluminum foil to prevent any light-activated deterioration of the compounds.

4.2.2. Multicompound standard - Weigh exactly 5 mg of each PNA (reagent 3.2.6.) into separate 30-ml beakers. Transfer quantitatively to one 100-ml volumetric flask, dilute to volume with spectranalyzed chloroform (concentration 50 µg/ml). Use this solution to determine the recovery factor for each compound.

4.3. Spectrophotometer parameters

4.3.1. Instrument parameters for ultraviolet range 250-350 nm.

- 4.3.1.1. Water - On
- 4.3.1.2. Power - On
- 4.3.1.3. Master - On
- 4.3.1.4. Scan speed-10 Å/sec.
- 4.3.1.5. Chart - On
- 4.3.1.6. Pen - On
- 4.3.1.7. Slit - On
- 4.3.1.8. Slit control - 25
- 4.3.1.9. Source - UV
- 4.3.1.10. IR detector - Out
- 4.3.1.11. Selector - UV
- 4.3.1.12. Shift knob - Out
- 4.3.1.13. Baseline - adjusted to keep the spectrum on the chart.

4.3.1.14. Absorbance screens - Use if necessary in the reference path with highly concentrated solutions to keep the peak and the baseline on the chart. These screens shift the effective range of the recorder with No. 1 causing the greatest downward shift and No. 3 the least downward shift.

4.3.2. Instrument parameters for the visible range 350-450nm.

4.3.2.1. See paragraphs 4.3.1.1. through 4.3.1.8. and 4.3.1.12. through 4.3.1.14.

4.3.2.2. Source - Vis

4.3.2.3. IR detector - Out

4.3.2.4. Selector - Vis

4.4. Absorptivity determinations

4.4.1. Transfer approximately 3 ml of the 1 $\mu\text{g}/\text{ml}$ pyrene solution (paragraph 4.2.1.) to a UV-Vis cell. Fill the reference cell with n-pentane. The cell rack (apparatus 3.1.14.) may be used to hold cells while out of the instrument. Place the cells in the respective holders in the instrument, replace the lids securely. Record the spectrum between 250 and 450 nm under the conditions outlined in paragraph 4.3. Remove the sample cell from the instrument, discard the solution, and clean the cell with n-pentane by using the cuvette washer (apparatus 3.1.11.). Repeat these steps with the 2 $\mu\text{g}/\text{ml}$, the 4 $\mu\text{g}/\text{ml}$, and the 10 $\mu\text{g}/\text{ml}$ solutions of pyrene.

4.4.2. Repeat paragraph 4.4.1. for the other eight PNA's, running four scans for each compound. Some of the solutions may be too concentrated to obtain measurements of the larger peaks (off scale), however make a complete scan on each solution.

4.4.3. Draw the baseline as indicated in Figure 2. between the wavelengths indicated in Table II. Measure the baseline and maxima absorbances for each spectrum at the wavelengths indicated in Table II. Save all the spectra for additional data needed in paragraph 4.7.8. Run the benzo(a)pyrene spectra, but make no measurements at this time.

TABLE II		
	<u>Absorbance Baseline</u>	<u>Absorbance Maxima</u>
pyrene	330-340	334
fluoranthene	284-290	287
benzo(a)anthracene	282-290	287
chrysene	262-270	267
benzo(e)pyrene	328-335	331
perylene	430-440	434
benzo(k)fluoranthene	395-405	401
anthanthrene	418-423	420

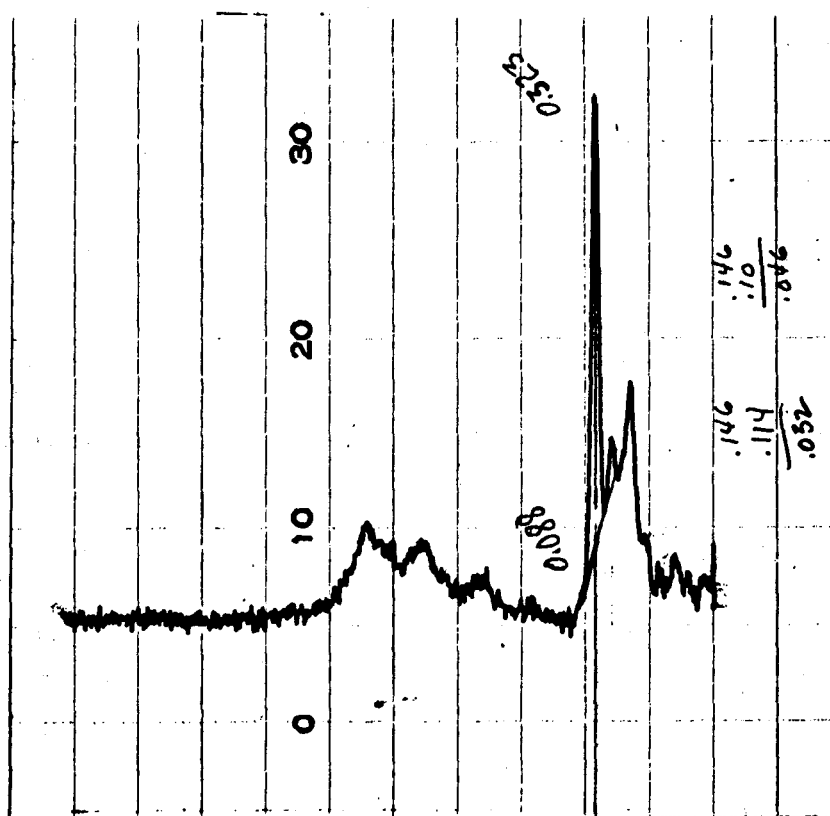


Figure 2. Absorption Spectrum of Fluoranthene (1 µg/ml).

4.5. Spectrophotofluorometer parameters

- 4.5.1. Optical unit power switch - On
- 4.5.2. Xenon power supply switch - On
- 4.5.3. Xenon lamp - Ignited
- 4.5.4. Chopper switch - On
- 4.5.5. HV control - Manual

4.5.6. Slits - cell compartment 1.0 mm emission and 1.0 mm excitation; blank slit out; and photomultiplier entrance position - 2.

4.5.7. Response - 1.

4.5.8. Monochromator scan - Off

4.5.9. Wavelengths setting - Pour approximately 1 ml of the benzo(a)-pyrene solution (10 μ g/ml) into a 2-oz bottle. Allow the solvent to evaporate in the hood. Add 10-15 ml of sulfuric acid, stir well. Fill the cell at least one-half full. Place the cell in the instrument, open the shutter, turn the HV control to ratio, set the excitation wavelength to ~520 nm and the emission wavelength to approximately 540 nm. Slowly, alternatingly, rotate the wavelength dials to maximize the meter reading. (The wavelength dials should not be set at the same wavelength.) After this maximization, do not readjust the wavelength settings during sample measurements. Return the HV control to manual and close the shutter.

4.5.10. Zero the instrument

4.5.10.1. Adjust the intensity meter to zero with the zero adjust vernier with the shutter closed and the sensitivity switch in zero adjust position.

4.5.10.2. Fill a cell with H₂SO₄, place in the instrument, open the shutter, turn the HV control to ratio, set the sensitivity switch to 0.1, the sensitivity vernier to 0, and use the blank subtract vernier to adjust the intensity meter to zero.

4.6. Response factor for benzo(a)pyrene

4.6.1. The manipulatory steps of adding acid and stirring should be performed rapidly, accurately, and reproducibly. Any alteration can greatly change the fluorometer reading and make the quantification questionable. The sulfuric acid-benzo(a)pyrene solution deteriorates quite rapidly.

4.6.2. Bubble nitrogen through the sulfuric acid contained in a reagent bottle for at least 10 minutes before use to remove oxygen and continue to bubble the nitrogen through the acid in the bottle throughout the test.

4.6.3. Set up the fluorometer as outlined in paragraph 4.5.

4.6.4. Transfer, by pipet, aliquots of the standard BaP solutions (paragraph 4.2.1.) to 2-oz bottles (see Table III for quantities). Allow the solvent to evaporate in the hood. Add the appropriate amount of H₂SO₄ (see Table III) to one bottle at a time, by using the 10-ml graduated cylinder, and stir well with a glass stirring rod to obtain good mixing. Immediately transfer the solution to a cell and place the cell in the instrument.

TABLE III

<u>BaP solution</u>		<u>µg BaP</u>	<u>Vol H₂SO₄</u>	<u>µg/ml</u>
<u>Vol.</u>	<u>Concn.</u>			
2	4 µg/ml	8	6	1.5
1	4 µg/ml	4	4	1
1	4 µg/ml	4	8	.5
1	4 µg/ml	4	16	.25
1	2 µg/ml	2	16	.125

4.6.5. Record the sensitivity setting and the meter reading.

4.6.6. Repeat paragraph 4.6.4. and 4.6.5. at least two more times to establish repeatability. Results should check better than 10%. Re-check zero adjustment (paragraph 4.5.10.) occasionally.

4.6.7. Prepare a plot of meter reading times sensitivity vs. concentration as in calculation 5.3. The curve should pass through zero and be linear to at least 1 µg/ml. If not, repeat paragraph 4.6.

4.7. Determination of liquid chromatography column recovery factors

4.7.1. Two or more columns are run with the known mixture (paragraph 4.2.2.) (2 ml is equivalent to 100 µg of each compound). These columns are used to determine the recovery factors (amount of compound recovered from the column in proportion to the amount added) and to ascertain which compounds elute in the same fractions. The recovery factor also will adjust for any loss due to handling necessary to quantify the nine compounds by absorption and fluorescent spectroscopy.

4.7.2. By using the triple beam balance (apparatus 3.1.10.), weigh the following materials (for each column to be run) into separate 2-oz bottles: 9.0 g of alumina, 0.5 g of silica gel, and 1.0 g of alumina. Cover the bottle openings with aluminum foil and cap securely. The weighing should be done under low humidity conditions, but not dry box conditions.

4.7.3. Deposition - Transfer, by pipet, 0.5 - 2.0 ml of the mixed standard solution (paragraph 4.2.2.) to the 1.0 gm of alumina. Allow the solvent to evaporate in the hood. Record the volume transferred.

4.7.4. Column packing - Attach the column securely to a ring stand at a convenient height to allow easy change of bottles under the column and to prevent effluent splashing out of the bottles. Tamp down a small piece of glass wool (apparatus 3.1.13.) immediately above the stopcock. This prevents the column packing from shifting out. Pour the 9.0 g of alumina through the funnel into the column, keeping the stopcock open. Tap

funnel and column lightly with a spatula or similar object to cause all of the alumina to fall into the lower portion of the column. Tamp down the alumina with the Plexiglass rod. Place a clean beaker under the column. Add ~130 ml of n-pentane to the column by using a dropper to allow the first 5-6 ml to run down the sides of the column in order not to disturb the alumina. By using the atomizer bulb with stopper, force air into the top of the column thereby forcing the n-pentane through the alumina which forces the entrapped air out the bottom of the column. Continue this, transferring n-pentane from the beaker to the column if necessary, until all noticeable air bubbles have been forced out of the alumina. Shut off the stopcock leaving the n-pentane level ~3-4 inches below the bottom of the reservoir. With the funnel add 0.5 g of silica gel slowly and evenly. Do not tap the column once the n-pentane has been added. With the dropper and n-pentane wash down any silica gel which has not fallen onto the alumina. Carefully stir the silica gel (not the alumina) with the steel rod until all air bubbles have risen from the silica gel. Drain n-pentane to a level ~1.5 inch above the silica gel. Adjust the n-pentane in the beaker to 100 ml. Pour from this beaker into the column until the solvent level is 3-4 inches below the reservoir. With the funnel, add the sample-containing alumina slowly and evenly such that no air is trapped. Do not tap the column. Wash down any stuck alumina with n-pentane and thoroughly rinse the sample bottle into the column with n-pentane. Rinse the funnel into the column with n-pentane and remove. Pour the remainder of the 100 ml of n-pentane into the reservoir. Wrap the packed portion of the column with aluminum foil.

4.7.5. Chromatographing the standards - Separate standard by use of solvent mixtures (reagent 3.2.8.) of increasing polarity (% ether).

Collect the standard-containing liquid eluting from the bottom of the column in 2-oz numbered bottles (15-20 ml per bottle). [The quantity of each solvent mixture added to the column is dependent on the alumina being used as packing material. After several exploratory columns have been run and adjustments in solvent volume made to attain the necessary compound separation, keep the solvent scheme constant for all columns run with that alumina. Either 100 or 150 ml of each solvent mixture has proved to be satisfactory. The order is: n-pentane, 3% ether-n-pentane, 6% ether-n-pentane, 9% ether-n-pentane, 12% ether-n-pentane, 15% ether-n-pentane, 18% ether-n-pentane, 25% ether-n-pentane, ether. Depending on the a

all of the solvent mixtures may not be needed to elute the compounds of interest. In that case, use the mixtures which are needed to obtain the separation.] Add each solvent volume (measured in a graduated beaker) when the preceding solvent level is ~2 inches above the packing and initially by use of a dropper and slow addition such that the packing is not disturbed by the solvent addition. Dry the collected fractions in the hood and box, cover, and store each set in the dark in the freezer.

4.7.6.1. Absorption spectroscopic measurements - Remove the box of bottles from the freezer and allow to equilibrate to room temperature. Set up the instrument as in paragraph 4.3. With a Pasteur pipet, 1-ml rubber bulb, and n-pentane, quantitatively transfer the material from the bottle to the cell. Use several rinses of n-pentane in order to more effectively transfer the material to the cell. Adjust the level in the cell with n-pentane to 3 ml. Stir with the dropper to have a homogeneous mixture. With n-pentane in the reference cell, record the spectrum over the range necessary to record the measuring absorption peak for all compounds present, see Table II. If the peaks of interest are off the chart two alternatives are possible. Place one of the screens (apparatus 3.1.3.) in the reference beam to shift both the baseline and peak. If this does not present a measurable peak, baseline and maximum, the sample must be diluted. With the dropper, remove liquid from the cell to the same bottle until the liquid level in the cell is at the 1-ml mark. Refill the cell with n-pentane to the 3-ml mark and stir to mix well. Record the spectrum and a 1x dilution. If the concentration is still too strong, make subsequent dilutions and note the number of dilutions on the spectrum. Quantitatively return the liquid in the cell to the same bottle, also rinse the dropper into the bottle, and clean the cell with the cuvette washer (apparatus 3.1.11.) and n-pentane. Set aside the bottles containing benzo(a)pyrene, after recording the absorption spectra, and allow the solvent to evaporate.

4.7.6.2. Fluorescent spectroscopic measurements - Analyze the bottles for BaP by fluorometry with H_2SO_4 (paragraph 4.6.). Adjust the volume of acid so that the meter reading times sensitivity is less than the upper linear limit established in calculation 5.3. Record the volume of acid, sensitivity, and meter reading on the form shown in Figure 4, and transfer for computer calculation to the form shown in Figure 8. (calculation 5.7.2.) or use this data for calculation 5.4.2.

4.7.6.3. Time Saving Steps - After several columns have been run and the type of separation determined, various bottles known to contain the same compounds can be combined before spectral measurements. This can be done to the extent that no additional interferences are created and that the resultant solution is of correct concentration range for the spectroscopy measurements. Dissolve the material in the bottles with n-pentane. Transfer the solution from several bottles into one bottle, quantitatively. Rinse the bottles several times. Allow the solvent to evaporate from the combination.

4.7.7. Spectra Workup - Locate the measuring peaks on each spectrum, (see Table I). Mark the baselines (Table I) (Figure 3.) and record the baseline absorbance, the maximum absorbance and the dilution for each compound on the computer form shown in Figure 8. By the peaks located on each spectra, determine the compounds that elute together.

4.7.8. Correction for overlapping compounds - If the separation on the column is not total and compounds overlap, corrections must be made in cases where the absorption spectra indicate interfering peaks. After preliminary columns and subsequent absorption spectra have been completed, ascertain the compounds which are eluted together from analysis of the spectra. Use the calibration spectra for individual compounds (paragraph 4.4.1. and 4.4.2.) to calculate the absorptivity (calculation 5.1. and 5.2.) for all compounds mutually present at the measuring wavelengths (Table I).

4.8. Sample Analysis

4.8.1. Prepare the column packing and pack the columns according to paragraphs 4.7.2. and 4.7.4.

4.8.2. Sample Deposition - Obtain the sample from the Soxhlet extraction (PSM-1013 or 1013a). Allow the solvent to evaporate to dryness in the hood. Avoid excess drying which may alter the sample. Dissolve the sample in a known volume of spectranalyzed chloroform. Transfer a known volume by pipet to the 1.0 g of alumina. Allow the solvent to evaporate in the hood. Select the volume of chloroform for dissolution and transfer such that 2 to 3 mg of the benzene solubles (PSM-1013 calculation 5. or PSM-1013a calculation 5.2.2.) are transferred to the 1.0 g of alumina. When the amount of benzene solubles is less than 3 mg, transfer the 1.0 g of alumina to the entire sample dissolved in approximately 5 ml of chloroform. Record the volumes on the computer form, Figure 8., or use in calculation 5.4.

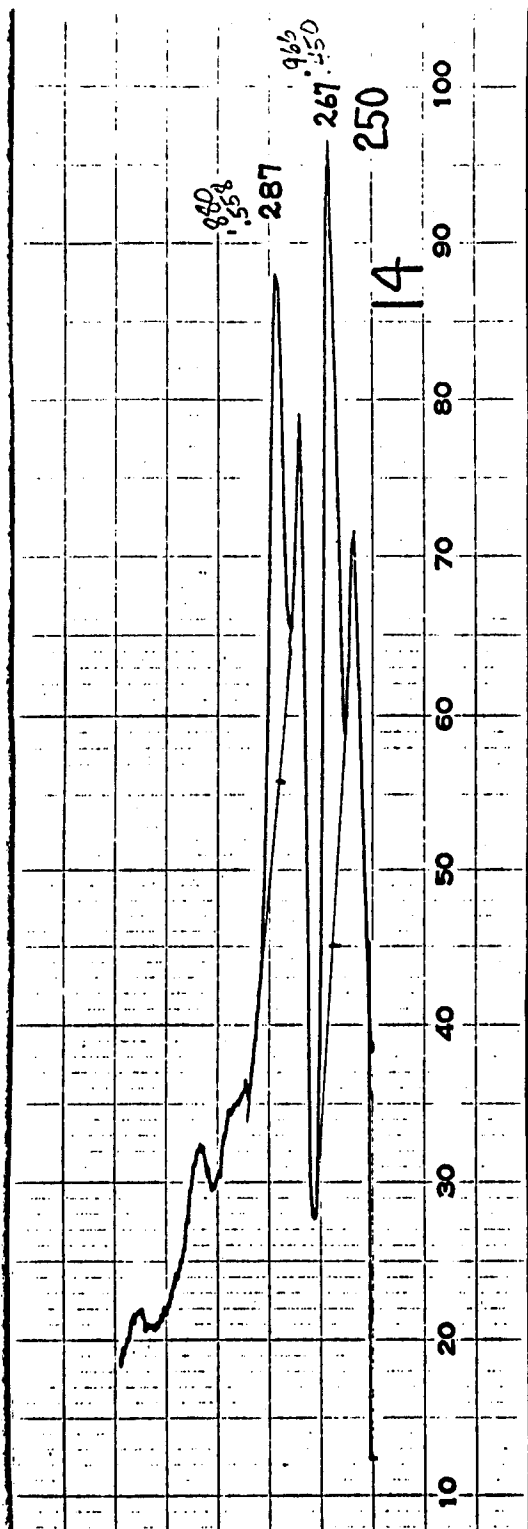


Figure 3. Absorption Spectrum of Fraction Containing Chrysene and Benz(a)anthracene.

4.8.3. Complete the sample analysis according to paragraphs 4.7.5. to 4.7.7.

4.9. Typical analysis

4.9.1. Solvent scheme

n-pentane	100 ml
3% ether	100
6% ether	100
9% ether	150
12% ether	100
18% ether	100

4.9.2. Elution order

1. pyrene	5. benzo(e)pyrene
2. fluoranthene	6. benzo(a)pyrene
3. benz(a)anthracene	7. perylene
4. chrysene	8. benzo(k)fluoranthene
9. anthanthrene	

4.9.3. Approximately 45 bottles were collected for each column. Fluoranthene and benz(a)anthracene must be completely separated since they are determined at the same wavelength. Up to ten columns can be run at the same time.

5. Calculations

5.1. Absorptivity

$$A_i / bc_i = a_i$$

where A_i = absorbance (maximum - baseline) (paragraphs 4.4.3. and 4.7.8.).

b = pathlength = 1 cm.

c_i = concentration in $\mu\text{g/ml}$ (paragraph 4.2.1.).

a_i = absorptivity at i concentration

5.2. Absorptivity average

$$\Sigma a_i / n = a$$

where a_i = absorptivity at i concentration (calculation 5.1.).

n = number of concentrations scanned.

a = absorptivity

5.3. Response factor for benzo(a)pyrene - Prepare a plot of meter reading (paragraph 4.6.5.) times sensitivity (paragraph 4.6.5.) versus concentration (paragraph 4.6.4. and Table III) on linear graph paper. The curve should pass through zero and be linear to at least 1 µg/ml concentration. Measure the meter reading times sensitivity at the 1 µg/ml concentration. This is the response factor for the fluorometric determination of benzo(a)pyrene. Take no readings on samples above the upper linear limit of the calibration curve.

5.4. Concentration

The following formulas can be used to determine the concentration of PNA's in a mixture when liquid chromatography has completely separated compounds which may interfere with each other for spectroscopic quantification.

5.4.1. From absorption spectroscopy

$$[\Sigma ((A/ab) \times D)] \times R \times W/P = c_a$$

where A = absorbance (maximum - baseline) (paragraph 4.7.7.).

a = absorptivity (calculation 5.2.).

b = cell path length - 1 cm.

D = dilution = number of milliliters in which the sample is dissolved for absorbance measurements (paragraph 4.7.6.1.) -- 3 = no redilution, 9 = 1x dilution, etc.

R = recovery factor = 1 for standards and readjusted (calculation 5.5.) for samples.

W = the total volume or weight (paragraph 4.7.3. for standards or 4.8.2. for samples).

P = the part, volume or weight, being analyzed (paragraph 4.7.3. for standards and 4.8.2. for samples).

c_a = concentration in whole sample, µg.

5.4.2. From fluorometry

$$[\Sigma (M \times S \times D)] \times (R/F) \times W/P = c_f$$

where M = meter reading (paragraph 4.6.5.).

S = sensitivity reading (paragraph 4.6.5.).

D = dilution = number of milliliters acid used for each bottle (paragraph 4.7.6.2.).

F = calibration value of 1 µg BaP / ml (calculation 5.3.).

R = recovery factor = 1 for standard and readjusted (calculation 5.5.) for samples.

W = the whole, volume or weight (paragraph 4.7.3. for standards and 4.8.2. for samples).

P = the part being analyzed, volume or weight (paragraph 4.7.3. for standards and 4.8.2. for samples).

c_f = concentration in whole sample, μg .

5.5. Recovery factors

$$C_c / C_d = R$$

where C_c = quantity chromatogrammed (paragraph 4.7.3.).

C_d = quantity calculated (calculation 5.4.).

R = recovery factor.

A separate recovery factor is determined for each of the nine compounds.

5.6. Multicomponent analysis

The absorbance at a specific wavelength is assumed to be the sum of the absorbances for each component that exhibits an absorbance at that specific wavelength. The resulting set of linear equations expressing the absorbance at each measured wavelength in terms of the absorptivity and the concentration of each of the nine polynuclear hydrocarbons was used to form a coefficient matrix. The coefficient matrix was inverted by standard matrix techniques. For each fraction the inverted matrix is multiplied by the column matrix formed from the measured absorbance for each wavelength. The column matrix formed by the multiplication contains the corrected (spectral interference) concentration for each component. Figure 6. is the computer program for the matrix inversion and Figure 7. is the matrix and the inverted matrix. Figure 9. is the computer program for calculation of the concentrations.

5.7. Computer Input

5.7.1. Matrix inversion program input (calculation 5.2. and paragraphs 4.4.3. and 4.7.8.).

Column 1-8 = Pyrene

Column 9-16 = Fluoranthene

Column 17-24 = Benz(a)anthracene

Column 25-32 = Chrysene

Column 33-40 = Benzo(e)pyrene

Column 41-48 = Perylene

Column 49-56 = Benzo(k)fluoranthene

Column 57-64 = Anthanthrene

Column 65-72 = Benzo(a)pyrene

Card 1 = 334 nm
 Card 2 = 287 nm
 Card 3 = 287 nm
 Card 4 = 267 nm
 Card 5 = 331 nm
 Card 6 = 434 nm
 Card 7 = 401 nm
 Card 8 = 420 nm
 Card 9 = fluorometer response factor (paragraph 5.3.).

All input data must include a decimal point.

Record absorptivities in corresponding locations, for example the absorptivity for benzo(e)pyrene at 287 nm goes in Column 33-40, Card 3. Column 1-8 and 9-16 and Card 1 and 2 contain data only for pyrene and fluoranthene since these compounds are completely separated from all the other compounds. Card 9 contains a datum only in column 65-72, the response factor for fluorometric determination of BaP (calculation 5.3.).

5.7.2. Concentration calculation program. Add the output deck from the matrix inversion program to the program deck. Add a table card containing the recovery factors for each compound (1.0 for standards, calculation 5.5. for samples) after the inverted matrix deck. Place the data cards after the table card. Place a card with a '1' punched in column 80 after the data cards to terminate the program.

5.7.2.1. Data input

Card 1
 Column 1 - 10 U.C.C. sample number
 Column 11 - 16 Government sample number
 Column 17 - 24 Date
 Column 25 - 32 Volume or weight of sample being analyzed
 Column 33 - 40 Volume or weight of whole sample.
 Column 47 - 48 Number of data cards - right justify
 Card 2-n n = number of data cards
 Column 1 Dilution for pyrene, 0=3 ml; 1=9 ml; 2=27 ml (paragraph 4.7.6.1.)
 Column 2 Dilution for fluoranthene
 Column 3 Dilution for benz(a)anthracene
 Column 4 Dilution for chrysene

Column 5	Dilution for benzo(e)pyrene
Column 6	Dilution for perylene
Column 7	Dilution for benzo(k)fluoranthene
Column 8	Dilution for anthanthrene
Column 9 - 12	Maximum at 334 (paragraph 4.7.7.) (implied decimal between 9 and 10)
Column 13 - 16	Baseline at 334 (implied decimal between 13 and 14)
Column 17 - 20	Maximum at 287 for fluoranthene (implied decimal between 17 and 18)
Column 21 - 24	Baseline at 287 for fluoranthene (implied decimal between 21 and 22)
Column 25 - 28	Maximum at 287 for benz(a)anthracene (implied decimal between 25 and 26)
Column 29 - 32	Baseline at 287 for benz(a)anthracene (implied decimal between 29 and 30)
Column 33 - 36	Maximum at 267 (implied decimal between 33 and 34)
Column 37 - 40	Baseline at 267 (implied decimal between 37 and 38)
Column 41 - 44	Maximum at 331 (implied decimal between 41 and 42)
Column 45 - 48	Baseline at 331 (implied decimal between 45 and 46)
Column 49 - 52	Maximum at 434 (implied decimal between 49 and 50)
Column 53 - 56	Baseline at 434 (implied decimal between 53 and 54)
Column 57 - 60	Maximum at 401 (implied decimal between 57 and 58)
Column 61 - 64	Baseline at 401 (implied decimal between 61 and 62)
Column 65 - 68	Maximum at 420 (implied decimal between 65 and 66)
Column 69 - 72	Baseline at 420 (implied decimal between 69 and 70)

Column 73 - 74	ml sulfuric acid used (right justify) (paragraph 4.7.6.2.)
Column 75 - 77	Sensitivity setting (implied decimal between 76 and 77)
Column 78 - 80	Meter reading (implied decimal between 79 and 80)

6. References

- 6.1. Health Lab. Sci., 7, 31, (1970).
- 6.2. Health Lab. Sci., 7, 45, (1970).
- 6.3. Parma Technical Center Notebook 572-4 and 572-8-1 to 36.

Sample # _____

[illegible]

6/19/72

```

// JOB
// FOR AL710
*IOCS(1443 PRINTER,CARD)
**MATRIX INVERSION AND PUNCH OUT
*ONE WORD INTEGERS
*LIST ALL
*NONPROCESS PROGRAM
      DIMENSION A(9,9),L(9),M(9)
      READ(2,1001)((A(I,J),J=1,9),I=1,9)
      WRITE(3,1004)
      WRITE(3,1002)((A(I,J),J=1,9),I=1,9)
      CALL MINV(A,9,D,L,M)
      WRITE(3,1002)((A(I,J),J=1,9),I=1,9),D
      WRITE(2,1003)A
1001 FORMAT(9(9F8.0//))
1002 FORMAT(9(E12.5,1X))
1003 FORMAT(5E16.8)
1004 FORMAT(1H1)
      CALL EXIT
      END
// XEQ AL710
*CCEND

```

Figure 6. Computer Program for Matrix Inversion,

Figure 7. Matrix (Card 1-9) and Inverted Matrix (Card 10-19).

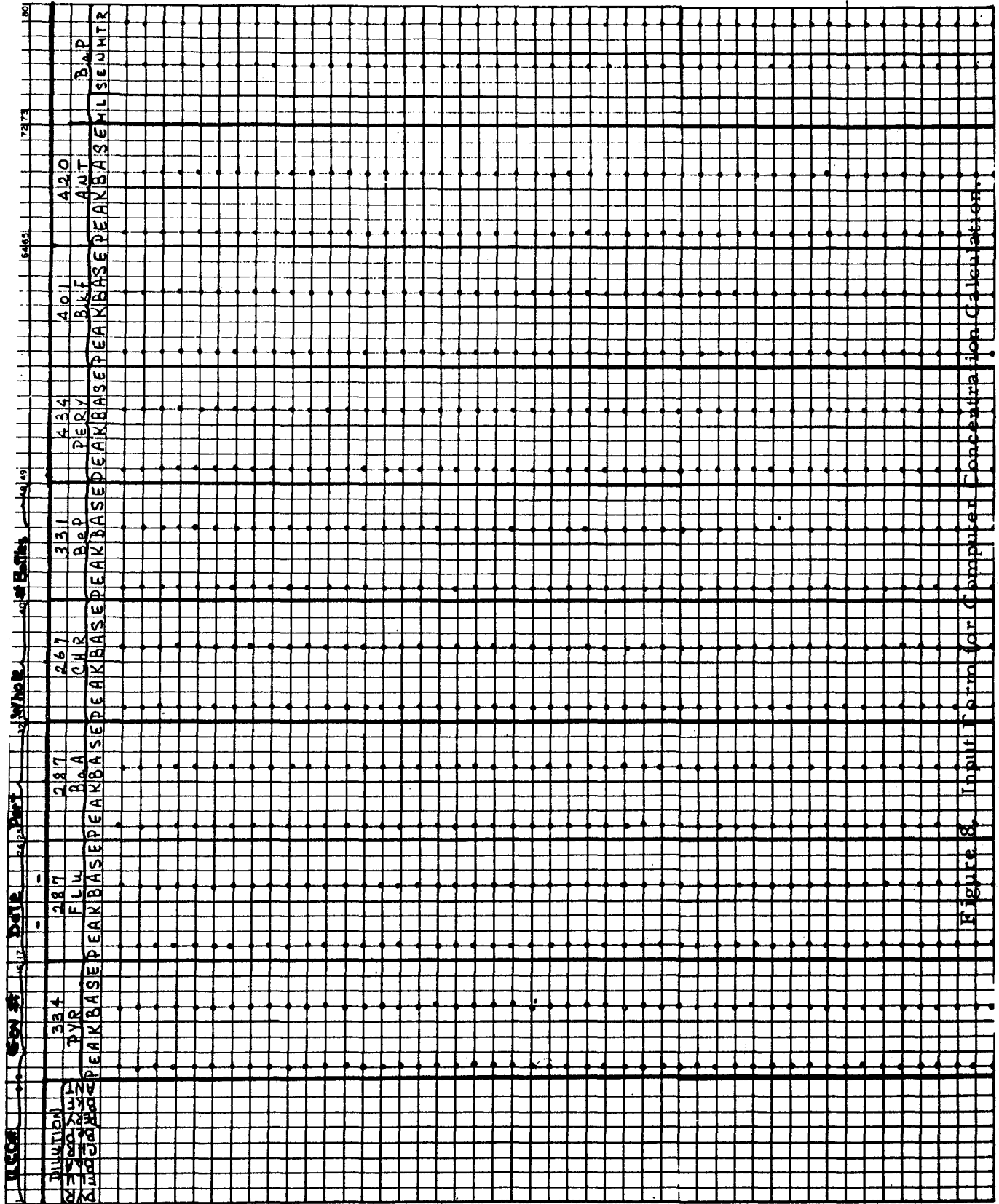


Figure 8. Input Form for Computer Concentration Calculation.

```

// JOB
// FOR AL711
*IOCS(1443 PRINTER,CARD)
**LIQUID CHROMATOGRAPHY CALCULATIONS
*ONE WORD INTEGERS
*NONPROCESS PROGRAM
  DIMENSION A(9,9),X(9),C(9),SX(9),IA1(5),IA2(3),IA3(4),RF(9),DF(6),
  11DF(8)
  DATA DF/3.0,9.0,27.0,81.0,243.0,729.0/
  READ(2,1002)A
1002 FORMAT(5F16.8)
  READ(2,1003)RF
1003 FORMAT(9F8.3)
180 ILNCT=0
  WRITE(3,1005)
1005 FORMAT('1 UCC NO      GOV NO   DATE      PYRENE   FLUORAN   B(A)
1A  CHRYSENE   B(E)P    PERYLENE B(K)F      ANT      B(A)P')
100 READ(2,1001)IA1,IA2,IA3,P,W,NB,LSTCD
1001 FORMAT(12A2,2F8.4,5X,13,31X,A1)
  IER=0
  IF(LSTCD-16448)190,200,190
200 DO 110 I=1,9
110 SX(I)=0.0
  DO 120 N=1,NB
  READ(2,1004)IDF,(C(I),X(I),I=1,6),D,S,C(9)
1004 FORMAT(8I1,16F4.3,2F0.2F3.1)
  C(9)=D*S*C(9)
  DO 130 I=1,8
  J=IDF(I)+1
  IF(J-6)130,130,140
130 C(I)=(C(I)-X(I))*DF(J)
  CALL GMPRD(A,C,X,9,9,1)
  CALL GMADD(X,SX,SX,9,1)
120 CONTINUE
  IF(IER)160,150,160
150 DO 170 I=1,9
170 SX(I)=SX(I)*RF(I)*W/P
  WRITE(3,1006)IA1,IA2,IA3,SX
1006 FORMAT(1X,5A2,4X,3A2,1X,4A2,9F10.2)
160 ILNCT=ILNCT+1
  IF(ILNCT-50)100,100,180
140 IER=1
  WRITE(3,1007)IA1,IA2,IA3,N
1007 FORMAT(1X,5A2,4X,3A2,1X,4A2,'ERROR IN DATA FOR BOTTLE ',I3)
  GO TO 120
190 CALL EXIT
  END

// FOR
*ONE WORD INTEGERS
  SUBROUTINE GMADD(A,B,R,N,M)
  DIMENSION A(1),B(1),R(1)
C    CALCULATE NUMBER OF ELEMENTS
  NM=N*M
C    ADD MATRICES
  DO 10 I=1,NM
10 R(I)=A(I)+B(I)
  RETURN
  END
// FOR
*ONE WORD INTEGERS
  SUBROUTINE GMPRD(A,B,R,N,M,L)
  DIMENSION A(1),B(1),R(1)
  IR=0
  IK=-M
  DO 10 K=1,L
  IK=IK+M
  DO 10 J=1,N
  IR=IR+1
  JI=J-N
  IB=IK
  R(IR)=0
  DO 10 I=1,M
  JI=JI+N
  IB=IB+1
10 R(IR)=R(IR)+A(JI)*B(IB)
  RETURN
  END
// XEQ AL711
*CCEND

```

	GMADD 1
	GMADD 2
	GMADD 3
	GMADD 4
	GMADD 5
	GMADD 6
	GMADD 7
	GMADD 8
	GMADD 9
	GMPRD 1
	GMPRD 2
	GMPRD 3
	GMPRD 4
	GMPRD 5
	GMPRD 6
	GMPRD 7
	GMPRD 8
	GMPRD 9
	GMPRD 10
	GMPRD 11
	GMPRD 12
	GMPRD 13
	GMPRD 14
	GMPRD 15
	GMPRD 16
	GMPRD 17

Figure 9. Computer Program for Concentration Calculation.

PARMA STANDARD TEST METHODS
UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM- 1014	ANALYSIS Composite Emission Index
RANGE Not Applicable	KEY REAGENT Iso-octane
PRECISION Not Applicable	MATRIX Airborne Particulates Collected on Air Sampling Filters
DATE ISSUED 12/8/71	DATE REVISED © 700001

COMPOSITE EMISSION INDEX OF VOLATILE MATTER
COLLECTED ON AIR SAMPLING FILTERS

1. Purpose and Limitation

1.1. This method is designed to photometrically and fluorometrically characterize (emission index) the iso-octane soluble polynuclear aromatic compounds and other organic compounds that are obtained from the material collected on air sampling filters.

1.2. This method is limited by the emission index of the reagents used. A reagent blank is carried through the entire procedure to ensure that the reagents do not significantly interfere.

2. Principle of Method

2.1. The soluble matter in airborne particulates which was collected on the air sampling filters is extracted with cyclohexane using the continuous cycling process of the Soxhlet extractor.

2.2. The cyclohexane extraction is partitioned with dimethylsulfoxide (DMSO) - phosphoric acid (H_3PO_4) mixture. The DMSO- H_3PO_4 extraction is partitioned with iso-octane.

2.3. The following spectra are obtained on the iso-octane extract: ultraviolet-visible from 200-600 nm; fluorometric emission from 300-500 nm with excitation at 350, 400, 450 nm; fluorometric excitation from 300-500 nm with emission at 350, 400, 450 nm.

3. Apparatus and Reagent

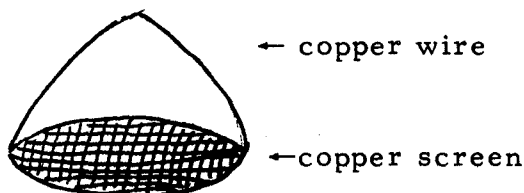
3.1. Apparatus

3.1.1. Soxhlet extractor apparatus - Six 250-ml size, Fisher Scientific, catalogue No. 9-551B or equivalent.

Preceding page blank

3.1.2. Extraction heater and support - Six position, Fisher Scientific, catalogue No. 9-678 or equivalent.

3.1.3. Copper Basket - A copper basket is fabricated by cutting a copper screen (approximately 40 mesh) into 35-mm diameter circles. Two single strand copper wires are attached to the screen to form handles. This basket is used to support the filter(s) in the Soxhlet extraction chamber (see drawing).



3.1.4. Miscellaneous - Tweezers, one 4 inch and one 10 inch size; ring stand with one large ring positioned directly above a smaller ring; Carborundum boiling chips; filter paper 12 1/2 cm; 3 plastic washing bottles; aluminum foil.

3.1.5. Glassware-six 400-ml, 250-ml, and 30-ml beakers; one 2000-ml beaker; one 2000-ml and eighteen 500-ml separatory funnels with suitable support racks; six 60° filtering funnels; three 250-ml, one 50-ml, two 500-ml, and one 1000-ml graduates; and one large glass stirring rod.

3.1.6. Air Manifold - containing 6 valves with glass tubes. Place in a well-ventilated hood.

3.1.7. UV lamp - long wavelength 3660 Å, Fisher Scientific, catalogue No. 11-984-1 or equivalent.

3.1.8. Scanning ratio spectrophotofluorometer - American Instrument Co., Model SP-F or equivalent. (The ratio mode was not necessary for this method. Use of this instrument in the manual mode is described in paragraph 4.5.)

3.1.9. X-Y recorder - American Instrument Co., No. 1620-855 or equivalent.

3.1.10 Recording spectrophotometer - Applied Physics Corporation, Cary Model 14 or equivalent.

3.1.11. Water deionizer - mixed bed ion exchanger for purifying water, such as Crystalab Deionizer.

3.1.12. Wrist action shaker - for shaking separatory funnels, Fisher Scientific, catalogue No. 14-260 or equivalent.

3.1.13. Drying Oven - 110°C, such as Fisher Scientific Catalogue No. 13-244-1 or equivalent.

3.1.14. Desiccator - plain, 100-150 mm diameter containing indicating desiccant, Fisher Scientific catalogue No. 8-636 or equivalent.

3.2. Reagents

3.2.1. Cyclohexane and iso-octane - Spectranalyzed, available from Fisher Scientific.

3.2.2. Dimethylsulfoxide - certified ACS grade.

3.2.3. Phosphoric acid 85% - certified ACS grade.

3.2.4. Sodium sulphate (anhydrous) - certified ACS grade, either powder or granular. Dry at 110°C overnight. Store in a desiccator.

3.2.5. Nitric acid and methyl alcohol for cleaning glassware.

3.2.6. Dimethylsulfoxide - phosphoric acid (DMSO-H₃PO₄) mixture

3.2.6.1. Preparation of mixture - Using a 1000-ml graduate, add 800 ml of DMSO to a 2000-ml beaker. Slowly add 200 ml of H₃PO₄ while stirring with a large stirring rod. Place the beaker in a cold water bath to cool. Stir occasionally to ensure mixing.

3.2.6.2. Pre-equilibration of DMSO-H₃PO₄ mixture - Using a 500-ml graduate, transfer 500 ml of the mixture (reagent 3.2.6.1.) to a 2000-ml separatory funnel. From another 500-ml graduate add 500 ml of cyclohexane. Close the separatory funnel and mix. Release the pressure after mixing. Shake for 2 minutes, releasing the pressure about every 30 sec. Allow the layers to separate. Transfer the DMSO-H₃PO₄ phase (lower portion) to a capped large storage bottle. Pour cyclohexane phase from the top of the separatory funnel into waste container. Repeat extraction for the remaining 500 ml of DMSO-H₃PO₄ mixture (reagent 3.2.6.1.). Transfer the second 500-ml portion of DMSO-H₃PO₄ to the capped storage bottle.

4. Procedure

4.1. Preliminary cleaning of Soxhlet extractor glassware.

4.1.1. Using concentrated HNO₃ in a washing bottle, rinse each part of the Soxhlet extractor. Rinse thoroughly with tap water. Dry the outside of each part with a lint-free tissue. Rinse the inside with methyl alcohol. Air dry to remove the excess alcohol.

4.1.2. Add 200 ml of cyclohexane and 5 to 10 boiling chips to each extraction flask. Assemble the Soxhlet extractor including the copper basket. Apply heat and continue heating for 5 hours after the first cycle of the slowest heater.

4.1.3. Turn off heat and discard the cyclohexane and boiling chips.

4.2. Preliminary cleaning of other glassware. (Beakers, separatory funnel, filtering funnels, graduates, etc.)

4.2.1. Rinse each item of glassware with a few ml of concentrated HNO_3 dispensed from a washing bottle. Rinse well three times with distilled water and finally with deionized H_2O . Invert to drain away as much H_2O as possible. Rinse with methyl alcohol and air dry.

4.2.2. By means of the UV light (paragraph 3.1.7.), check each item for fluorescence. If fluorescent material is found repeat paragraph 4.2.1., using hot HNO_3 . If no fluorescence is observed, glassware is now ready for use.

4.3. Soxhlet extraction with cyclohexane - samples are usually analyzed in lots of six.

4.3.1. Number the Soxhlet extraction chambers and flasks "1" through "6". Renumber the cassette samples "1" through "6". Make a record of the old cassette numbers and correlate to the new numbers, "1" through "6". (This will eliminate labeling the flasks with very long cassette codes.)

4.3.2. A blank is run periodically, especially if new reagents are employed, to ensure that the reagents do not interfere. A blank is run according to paragraphs 4.3.3. through 4.9.6. except that no filters are placed into the Soxhlet chamber (paragraph 4.3.3.).

4.3.3. Place 200 ml of cyclohexane in each extraction flask along with 5 to 10 boiling chips. Place cassettes in front of corresponding extraction flask. Open cassette number one. Using the small tweezers and micro-spatula, remove all filters above the bottom support filter. (The number and type of filter may vary. A silver filter usually is located next to the filter support. The silver filter is used both as a sample and as a support for the other filters. If a silver filter is not contained in the cassette, use a silver filter previously extracted in the Soxhlet extractor.) Carefully transfer the filters to the copper basket. Using the large tweezers, lower the basket into the Soxhlet chamber. Assemble the Soxhlet apparatus. Repeat for each sample. This portion of the procedure may be performed the day prior to extraction.

4.3.4. Turn the heaters on maximum setting. Extract for 5 hours after the slowest sample cycles once. Turn the heaters off. Flasks may or may not be emptied immediately.

4.3.5. In a well-ventilated hood, place six 400-ml beakers, numbered to correspond with flask numbers. Remove the Soxhlet chamber and extraction flask from heater. Tilt so as to allow as much cyclohexane as possible to drain from the Soxhlet chamber into the extraction flask. Separate the Soxhlet chamber from the extraction flask. Using the large tweezers, remove the copper basket containing the filters from the Soxhlet chamber. Using a washing bottle containing cyclohexane, rinse the Soxhlet chamber at least three times. Pour the washings into the appropriate 400-ml beaker. Transfer the entire contents of the extraction flask (minus the boiling chips) into the appropriate beaker. Rinse the extraction flask three times with cyclohexane and transfer the rinsings to the appropriate beaker. Repeat for each sample.

4.3.6. Place uncovered beakers under the air manifold. Evaporate to approximately 50 ml. Occasionally rinse the walls of the beakers with cyclohexane to remove any adhering particles.

4.4. Extraction of cyclohexane with iso-octane.

4.4.1. Assemble eighteen 500-ml separatory funnels, six 250-ml beakers and six filtering funnels. Close all stopcocks on the separatory funnels. Number the eighteen separatory funnels "1-1, 1-2, 1-3, 2-1, 2-2, 2-3 ---- 6-3." Three separatory funnels are required for each sample.

4.4.2. By means of a cyclohexane wash bottle, carefully transfer sample number 1 from the beaker to separatory funnel number 1-1. Rinse the beaker 3 times with cyclohexane. Then transfer rinsings to the separatory funnel. Add 50 ml of DMSO- H_3PO_4 (reagent 3.2.6.1.) to the sample. Shake for 2 min. either manually or mechanically. Allow the layers to separate and transfer the DMSO- H_3PO_4 (lower portion) to separatory funnel number 1-2. Repeat the DMSO- H_3PO_4 addition and extraction two more times, collecting all of the DMSO- H_3PO_4 in the separatory funnel number 1-2. Discard the cyclohexane phase. Rinse the number 1-1 separatory funnel with iso-octane and discard the rinsings.

4.4.3. To the number 1-2 separatory funnel containing the combined DMSO- H_3PO_4 , add 150 ml of H_2O . Swirl to ensure mixing. Add 50 ml of iso-octane. Shake for 2 min. Transfer the DMSO- H_3PO_4 (lower phase) to the number 1-1 funnel. Transfer the iso-octane phase to separatory funnel number 1-3. By alternating funnels 1-1 and 1-2 extract and separate 2 more times. Collect all of the iso-octane in the separatory funnel number 1-3. After the third separation, discard

DMSO- H_3PO_4 . To the iso-octane phase, add 170 ml of deionized H_2O . Shake for 2 minutes. Transfer the H_2O phase (lower portion) to a waste beaker. Dry the separatory funnel stem with a Kimwipe or a folded filter paper.

4.4.4. Prepare a filtering funnel (for water removal) in the following manner: insert one piece of folded filter paper into the funnel and fill with approximately 35 g of Na_2SO_4 . Rinse the Na_2SO_4 with iso-octane. Place the filtering funnel in a small ring holder and the separatory funnel in a large ring holder. Position a 250-ml beaker beneath the filtering funnel. Open the separatory funnel stopcock, and carefully drain the iso-octane into the filtering funnel until the funnel is full. Close the stopcock. Continue until all of the iso-octane has been filtered through the Na_2SO_4 and is collected in the 250-ml beaker. Using a washing bottle, rinse the separatory funnel three times with small amounts of iso-octane. Drain the washings into the filtering funnel so that it will be collected in the 250-ml beaker.

4.4.5. Repeat paragraphs 4.4.1. through 4.4.4. for all samples.

4.4.6. Place the uncovered beakers under the air manifold. Evaporate to approximately 25 ml. Carefully transfer the contents of each beaker to 30-ml beakers. Using a washing bottle containing iso-octane, rinse the 250-ml beaker 3 times and combine the rinsings in the 30-ml beaker. Evaporate to 15 ml. Cover the beakers with aluminum foil.

4.5. Spectrophotofluorometer parameters

4.5.1. HV control switch - manual.

4.5.2. Chopper switch - on.

4.5.3. HV control vernier - adjust so that HV control meter reads 0.6 KV. (Vernier is approximately 8.35.)

4.5.4. Response - 1.

4.5.5. Slits - cell compartment, 1.0 mm emission and 1.0 mm excitation; blank slit "in" (for blocking ratio reference beam); and photomultiplier entrance, position 2.

4.5.6. X-Y recorder - on, load position.

4.6. Zero instrument

4.6.1. Adjust relative intensity meter needle to zero with zero adjust.

4.6.2. Set sensitivity switch to .1 position and set relative intensity needle to zero with blank subtract (L and fine control).

4.7. Fluorometric measurement of samples.

4.7.1. Fill the 10 mm cell approximately one half full with sample (paragraph 4.4.6.). Insert sample in cell block and replace housing. Open shutter (down). Set emission wavelength at 300 nm. Set excitation wavelength at 350 nm.

4.7.2. Emission spectra - Set recorder pen (up position) on zero using the X and Y adjustment. In order to record the entire spectrum on the graph, manually scan by turning the emission dial from 300 nm to 500 nm. If the fluorescence intensity needle goes off scale, decrease the sensitivity (example .1 to .3 etc.) until all fluorescent peaks are on scale.

4.7.3. For recording the emission spectra, set recorder pen on zero using the X and Y adjustment. Lower pen on the graph paper.

Turn scanning dial to emission. Scan from 300 nm to 500 nm. Raise pen to load position. Turn scanning dial off.

4.7.4. Record on the graph paper before removing; emission spectra, beaker number, date, sensitivity setting as MM and ex wavelength.

4.7.5. Obtain 3 emission spectra for each sample with excitation at 350 nm (as in paragraph 4.7.1.), 400 nm and 450 nm. Repeat paragraphs 4.7.2. through 4.7.4. using 400 nm and 450 nm as the excitation wavelengths.

4.7.6. Excitation spectra - Obtain in the same manner as the emission spectra with the following exceptions. Paragraph 4.7.1. - Set excitation wavelength at 300 nm and emission wavelength at 350 nm. Paragraph 4.7.2. - Using the Y adjustment of the recorder, set pen at the relative intensity (example 30, 50, 70, etc.) that will allow the entire spectrum to be recorded. (See Figure 2.) A zero or baseline above 80 relative intensity units is not recommended. Manually scan by turning the excitation dial from 300 nm to 500 nm.

4.7.7. For recording the excitation spectra lower pen to down position. Turn scanning dial to excitation. Scan from 300 nm to 500 nm. Record appropriate excitation data on the graph before removing from the recorder.

4.7.8. Obtain 3 excitation spectra for each sample with emission at 350 nm (as in paragraph 4.7.6.), 400 nm, and 450 nm. Repeat paragraphs 4.7.6. and 4.7.7. to obtain the 400 nm and 450 nm emission spectra.

4.7.9. To change samples, follow this sequence. Close the shutter (up). Transfer sample to the original beaker. Rinse the cell 3 times with iso

octane. Discard the rinsings. Add new sample to cell. Insert the sample in cell block. Replace the housing. Open the shutter (down).

4.7.10. Repeat paragraphs 4.7.1. through 4.7.8. for each sample.

4.7.11. Identification of graphs. Letter each graph showing the following: beaker number, Parma analytical number, cassette number, solvent, MM, sensitivity, PM tube, lamp, temperature, date, observer, slit size, sample tube and graph number. (see Figures 1 and 2 for examples).

4.8. Spectrophotometer parameters

4.8.1. Instrument parameters for UV range 200-350 nm.

4.8.1.1. Scan Speed - $10 \text{ \AA/sec.}$

4.8.1.2. Chart - On

4.8.1.3. Pen - On

4.8.1.4. Slit - On

4.8.1.5. Slit Control - 25

4.8.1.6. Source - UV

4.8.1.7. IR detector - Out

4.8.1.8. Selector - UV

4.8.1.9. Shift Knob - Out

4.8.2. Instrument parameters for visible range, 350-600 nm.

4.8.2.1. See paragraphs 4.8.1.1. through 4.8.1.5. same parameters as UV range.

4.8.2.2. Source - Vis

4.8.2.3. IR detector - Out

4.8.2.4. Selector - Vis

4.8.2.5. Shift Knob - Out

4.9. Photometric measurement of samples

4.9.1. Fill one 10-mm cell with pure iso-octane from a wash bottle. Wipe the sides of the cells with a Kimwipe. Place the cell in the reference chamber (back) of instrument. Replace the housing.

4.9.2. Dilute the samples (paragraph 4.7.9.) to approximately 25 ml with iso-octane. Fill the second 10-mm cell with the sample. After wiping the cell with a Kimwipe, place in the front chamber of the instrument. Replace the housing. Turn on the master switch. Using a fast scan speed, advance the wavelength to 350 nm.

4.9.3. Set instrument for UV range. (see paragraph 4.8.1.). At a fast speed, decrease the wavelength to below 200 nm (approximately 195

Entire scan must be recorded on the graph. If both pens go off scale before reaching 200 nm, turn scan off immediately. Turn off the master switch. (The master switch must be off before housing is removed from the instrument.) Remove the sample from the chamber. Pour out approximately 1/2 of the sample. Fill the cell with iso-octane from a wash bottle. Replace the sample in the chamber. Replace housing. Turn on the master switch. Continue decreasing the wavelength to below 200 nm (approximately 195 nm). If both pens still go off scale, repeat the dilution procedure.

4.9.4. Once the fast scan is completed with one pen staying on the graph, slowly advance the wavelength to exactly 200 nm. If necessary manually advance the chart to the point where the pen is exactly on a line. Mark the line as 200 nm. Record the sample number (beaker). Lower the pen. Set scan speed at $10 \text{ \AA}/\text{sec}$. Turn on the wavelength switch and chart switch simultaneously. Advance the wavelength to 350 nm.

4.9.5. At 350 nm turn the wavelength and chart switch OFF. Lift the pen. Reset the instrument for the visible range (see paragraph 4.8.2.). Manually advance the chart to a point where the pen is exactly on a line. Lower the pen. Mark the line as 350 nm. Continue the scan to 600 nm.

4.9.6. Repeat paragraphs 4.9.1. through 4.9.5. for each sample.

4.9.7. Identification of graphs

4.9.7.1. Label the graphs as indicated in Figure 3.

5. Reference

5.1. Union Carbide Corporation - Parma Technical Center Notebook 572-5.

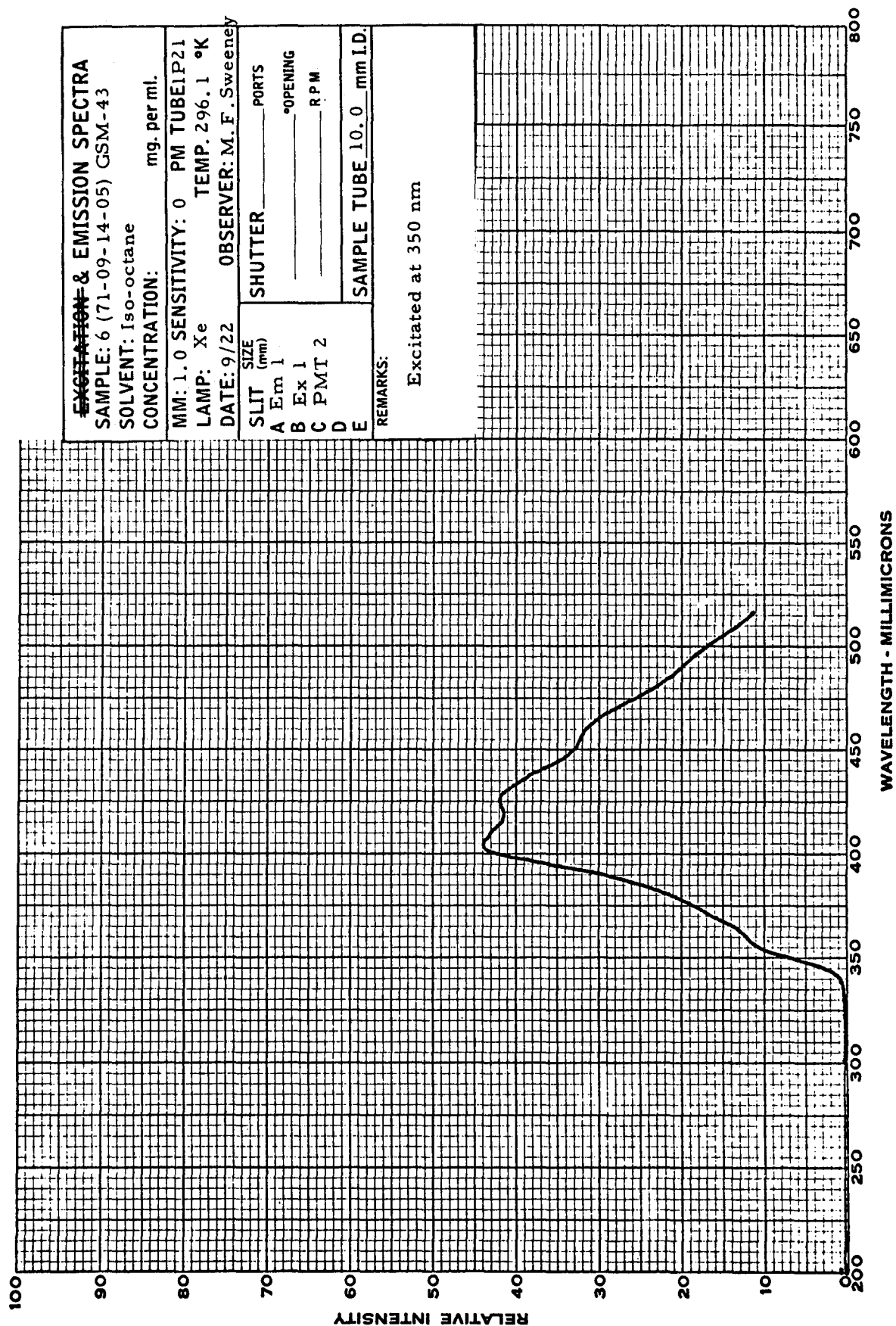


Figure 1. Emission Spectra with Excitation at 350 nm.

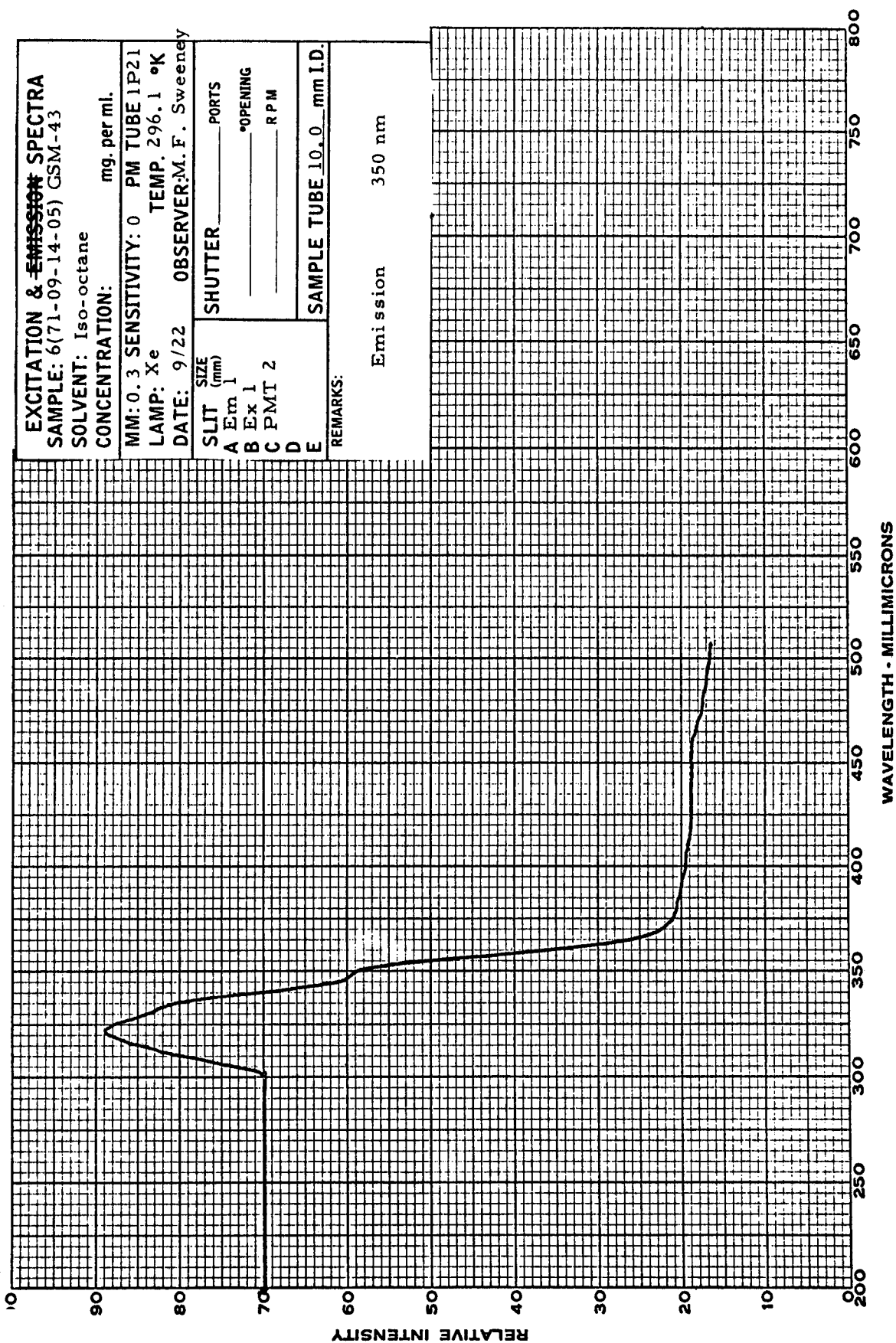


Figure 2. Excitation Spectra with Emission at 350 nm.

Graph No. = 70-G
6(71-09-14-05) GSM-43
Cary 14
Cell = 10 mm
Scan Speed - 10 Å/sec.
VS- Iso-octane
Diluted

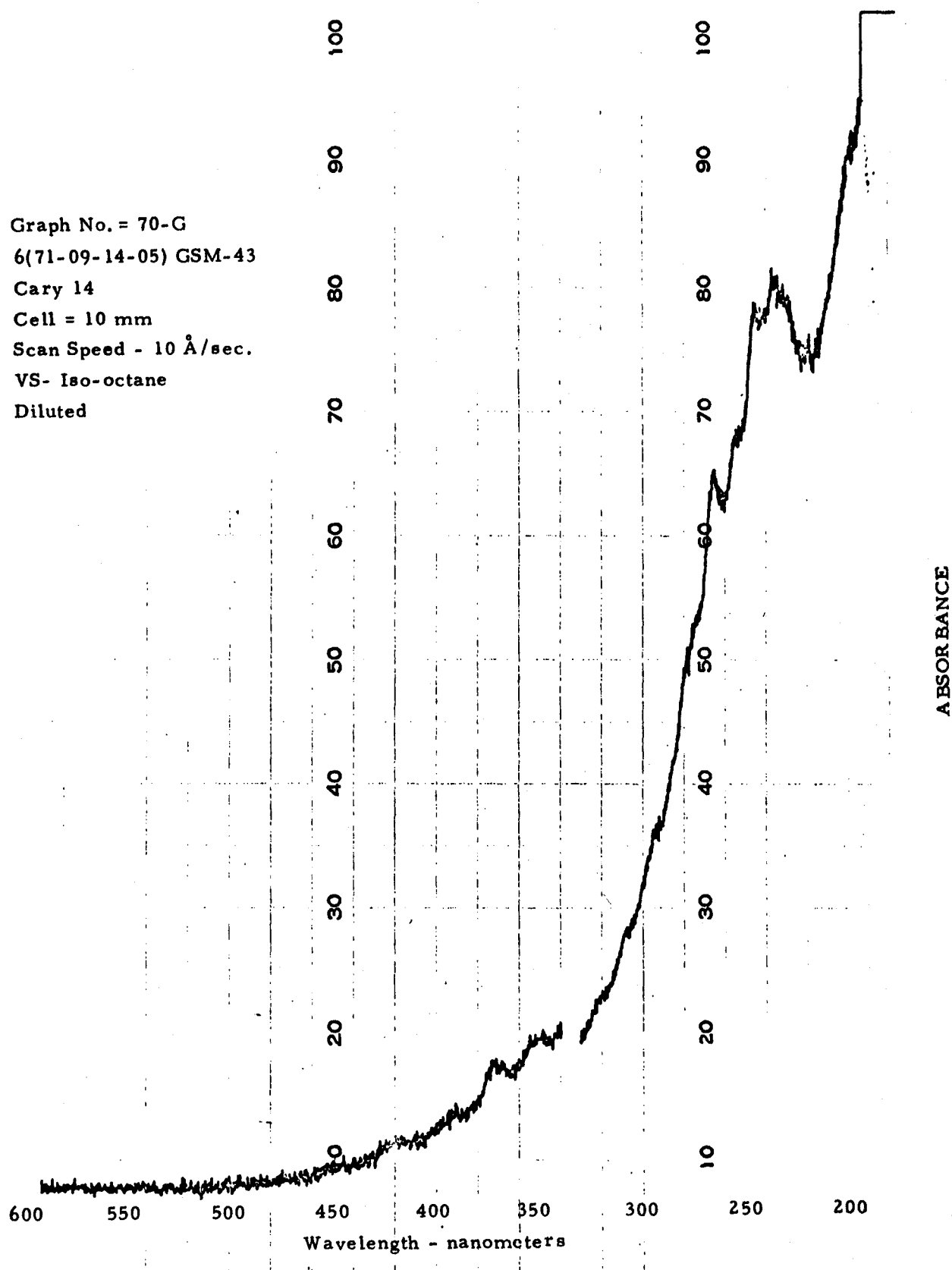


Figure 3. UV-Vis Spectra (200 nm - 600 nm).

PARMA STANDARD TEST METHODS
UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM-1014a	ANALYSIS Composite Emission Index
RANGE Not Applicable	KEY REAGENT Iso-octane
PRECISION Not Applicable	MATRIX Airborne Particulates Collected on Hi-Vol (Glass Fiber) Filters
DATE ISSUED 6/5/72	DATE REVISED 9 700001

COMPOSITE EMISSION INDEX OF VOLATILE MATTER
COLLECTED ON HI-VOL (GLASS FIBER) FILTERS

(This procedure utilizes PSM-1014 and 1013a)

1. Purpose and Limitations

- 1.1. This method is designed to accommodate the large amount of air particulates collected on the Hi-Vol (Glass Fiber) filters.
- 1.2. The cyclohexane extract is used for both the emission index determination and the polynuclear aromatic determination by gas chromatography (see PSM-1016). The samples are stored away from light and heat in a freezer to inhibit deterioration. The Soxhlet apparatus is covered with aluminum foil during extraction.
- 1.3. The composite emission index method is a qualitative method. The calculations given in Section 5 are used merely as a guideline to obtain the approximate portion of the sample needed. Dilution of the sample will enable the most intense fluorescent peak to be recorded. A concentrated sample will not allow light to pass through, producing a straight line.
- 1.4. See also "Purpose and Limitations" in PSM-1014, Section 1.

2. Principle of Method

- 2.1. The Hi-Vol filters are divided according to PSM-1013a (paragraph 4.2.). The portion set aside for cyclohexane extraction is used for this method.
- 2.2. See PSM-1014, Section 2, "Principle of Method."

2.3. The extract is divided equally between the emission index determination and the PNA determination by GC (see PSM-1016).

3. Apparatus and Reagents

3.1. Apparatus

3.1.1. See PSM-1014, paragraphs 3.1.1., 3.1.2., 3.1.5., omit the 400 ml beakers and replace with 12 wide-mouth glass jars, capacity approximately 200 ml. All other glassware is needed.

3.1.2. See PSM-1014, paragraphs 3.1.6. through 3.1.14.

3.1.3. Extraction thimbles - alundum, RA98 course-12. Available from Fisher Scientific Co., Cat. No. 9-661-C or equivalent. Label with Coors ceramic marking ink.

3.1.4. Furnace - Temco, Model No. F-1740 - or equivalent for cleaning alundum thimbles.

3.1.5. Indicating Pyrometer Controller for Furnace - Capable of regulating $\pm 20^{\circ}\text{C}$ @ 600°C - available from Fisher Scientific Co., Cat. No. 10-557-13, or equivalent.

3.1.6. Freezer - Storage Cabinet - Fisher Scientific Co., Cat. No. 13-988-35 or equivalent.

3.1.7. Copper Screen - (approximately 40 mesh) - cut in circles with a 35 mm diameter.

3.1.8. Miscellaneous - Tweezers, 10 inch size; furnace tongs; Carborundum boiling chips; plastic washing bottles; aluminum foil; asbestos, sheets approximately 12" square; aluminum tray, 9 x 9" lined with a paper towel.

3.2. Reagents

3.2.1. See PSM-1014, paragraphs 3.2.1. through 3.2.6.

4. Procedure - Samples may be analyzed in lots of 6.

4.1. Preliminary cleaning of alundum extraction thimbles

4.1.1. Use the furnace tongs to place the 6 alundum thimbles in the 600°C furnace. Heat for at least one hour. Remove the thimbles from the furnace with the tongs, and place on the asbestos to cool. Store in a desiccator.

4.2. Preliminary cleaning of Soxhlet extractor glassware

4.2.1. See PSM-1014, paragraph 4.1.1.

4.2.2. Add 200 ml of cyclohexane and 5 to 10 boiling chips to each extraction flask. Place a copper circle and then an alundum thimble in each extraction chamber. Assemble the Soxhlet extractor. Apply heat and continue heating for 5 hours after the first cycle of the slowest heater. Turn off the heaters.

4.2.3. In a well-ventilated hood, disassemble the Soxhlet extractor. Use the tweezers to remove the alundum thimble and place in the aluminum tray. Empty the extraction flask and discard the cyclohexane. Cover the Soxhlet chamber and extraction flask separately with aluminum foil. Attach foil with tape if needed. Remove the portion of the foil that will be in contact with the heaters.

4.2.4. Air dry the alundum thimble until the cyclohexane odor has disappeared. Repeat paragraph 4.1.1. The Soxhlet extractor and thimbles are now ready for use.

4.3. Preliminary cleaning of other glassware (bottles, separatory funnels, filtering funnels, graduates, etc.). See PSM-1014, paragraph 4.2.

4.4. Soxhlet extraction of sample with cyclohexane

4.4.1. Obtain samples that have been divided, weighed and inserted in the appropriate alundum thimble according to PSM-1013a, paragraph 4.2.7.

4.4.2. Also obtain the weight sheet (see PSM-1013a, Figure 1).

4.4.2. See PSM-1014, paragraph 4.3.2.

4.4.3. Place 200 ml of cyclohexane in each extraction flask along with 5 to 10 boiling chips. Use the tweezers to lower the alundum thimble containing the sample into the Soxhlet chamber. Assemble the Soxhlet apparatus. Repeat for each sample. This portion of the procedure may be performed the day prior to extraction.

4.4.4. Turn the heaters on maximum setting. Extract for 5 hours after the slowest sample cycles once. Turn the heaters off. Flasks may or may not be emptied immediately. Samples should not remain in the extractor for more than one hour.

4.4.5. In a well-ventilated hood, place 2 sets of 6 each, wide-mouth bottles, numbered to correspond with the sample numbers. One set of bottles is used for the emission index samples and the other set is used for GC samples.

4.4.6. Remove the Soxhlet chamber and extraction flask from the heater. Tilt to allow most of the cyclohexane to drain from the Soxhlet chamber into the extraction flask. In a hood separate the Soxhlet chamber from the extraction flask. Use the tweezers to remove the alundum thimble containing the sample from the Soxhlet chamber. Use a washing bottle containing cyclohexane to rinse the Soxhlet chamber at least three times. Pour the washings into a 250-ml graduate. Transfer the entire cont

of the extraction flask (minus the boiling chips) into the same graduate. Rinse the extraction flask three times with cyclohexane and transfer the washings to the same graduate. Measure the volume. Transfer one-half of the extraction liquid to the appropriate bottle for the emission index determination and the other half to the bottle for the GC analyses. Rinse the graduate four times, transferring 2 washings to each bottle. Cover each bottle top with aluminum foil and cap.

4.4.7. Repeat paragraph 4.4.6. for each remaining sample. If the samples are not analyzed immediately, cool and store in the freezer. If the emission index samples are analyzed immediately, proceed according to paragraph 4.4.8.

4.4.8. Emission index samples should be a light yellow color. If the samples are a light yellow, proceed as in paragraph 4.4.9. If the samples are a dark yellow to brown color the sample is too concentrated. An aliquot is taken. Transfer the concentrated sample to a 250-ml graduate. Dilute to 200 ml with cyclohexane. Stir with the long stirring rod to ensure mixing. Depending on the color intensity, transfer 25 ml or 50 ml to the appropriate graduate. Record this aliquot (either 25 ml or 50 ml) on weight sheet that accompanies each sample (see paragraph 4.4.1.). Proceed according to paragraph 4.5.

4.4.9. Place samples under the air manifold. Evaporate to approximately 50 ml. Occasionally rinse the walls of the beakers with cyclohexane to remove any adhering particles.

4.5. Cleaning of alundum thimbles for reuse

4.5.1. Discard filter and repeat paragraph 4.1.1.

4.6. Extraction of cyclohexane with iso-octane - see PSM-1014, paragraph 4.4.

4.7. Fluorometric Measurement of Samples - See PSM-1014, paragraphs 4.5. through 4.7.3.

4.7.1. If the spectrum is not a straight line but has fluorescent peaks, proceed according to PSM-1014, paragraph 4.7.4. If the recorded spectrum is a straight line, the sample is too concentrated and requires additional dilution. Close the shutter and remove the sample from the instrument. Place the cell on a flat surface. While holding a ruler (or a piece of marked cardboard) behind the cell, remove the sample to the 0.4 inch line using a medicine dropper. Fill to the 1.6 inch line with iso-octane from the washing bottle. Stir gently with the medicine dr

to ensure mixing. Return the cell to the instrument and proceed as in PSM-1014, paragraphs 4.7.2. through 4.7.5.

4.7.2. If the spectrum is not a straight line, record the dilution as "1" and proceed according to 4.7.3. If the spectrum is a straight line, repeat the dilution procedure as described in paragraph 4.7.1. Record the final number of dilutions after the spectrum ceases to be a straight line.

4.7.3. Excitation spectra - Proceed according to PSM-1014, paragraphs 4.7.6. and 4.7.7. If the spectra is a straight line, dilute the sample as described in paragraph 4.7.1. (The measurement of the excitation spectra usually requires more dilutions than the emission spectra.)

4.8. For the remainder of the procedure, see PSM-1014, paragraph 4.7.8.

5. Calculation and labeling of graphs

5.1. Samples that are not diluted after extraction

$$\frac{A \times 50}{C} = D$$

where

A = Weight of sample used for the cyclohexane extraction, g.
(Weight sheet, column 5, paragraph 4.4.1. - see PSM-1013a, Figure 1.)

C = Total weight of Hi-Vol filter, g, (column 6 weight sheet).

D = Per cent of total filter represented, before dilution.

5.2. Samples that are diluted after extraction

5.2.1. Dilution factor

$$\frac{E}{200} = F$$

where

E = Aliquot, either 25 ml or 50 ml (paragraph 4.4.8.).

F = Dilution factor

5.2.2. Sample percentage

$$D \times F \times (1/4)^n = G$$

where

D = Per cent of total filter represented before dilution.

(Calculation 5.1.)

F = Dilution factor (calculation 5.2.1.).

n = Number of 1 to 4 dilutions made in the fluorometer cell;
if n=0, $(1/4)^n = 1$ (paragraph 4.7.1.).

G = Per cent of total filter represented after dilution.

5.3. Label graphs according to PSM-1014, Figures 1, 2, and 3, except on Figures 1 and 2 label across the top of the graph the per cent of the total filter represented (paragraph 5.1. or 5.2.2.).

6. Reference

6.1. Union Carbide Corporation, Parma Technical Center Notebook 572-5 and 572-7.

PARMA STANDARD TEST METHODS

UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM- 1020	ANALYSIS Trace Metals (viz. Co, Cr, Cu, Mn, Ni and Zn)
RANGE μ g Range (Can be extended to mg range if sample is diluted for analysis)	INSTRUMENT Atomic Absorption Spectrophotometer
PRECISION Not Determined	MATRIX Airborne Particulates Trapped on Hi-Vol Filters (Glass Fiber)
DATE ISSUED 6/30/72	DATE REVISED 9700142

DETERMINATION OF TRACE METALS IN AIRBORNE PARTICULATES BY ATOMIC ABSORPTION SPECTROPHOTOMETRIC TECHNIQUES

(This procedure utilizes PSM-1013a)

1. Purpose and Limitations

- 1.1. This method is designed for determining trace metals in airborne particulates which have been trapped on Hi-Vol filters (glass fiber). Atomic absorption spectroscopy is employed to determine the following six trace metals: cobalt, chromium, copper, manganese, nickel, and zinc. The method could be expanded to include trace metals other than the six specified ones.
- 1.2. The determination of the six specified elements in the original 25-ml sample solution is limited by the sensitivity (μ g/ml) of the particular atomic absorption spectrophotometer being used: the more sophisticated models having the best sensitivity for each of the various elements.
- 1.3. Even though the method could be expanded to include additional trace metals, the actual number which can be determined is limited by the 25-ml sample volume. To analyze for more than eight metals would be difficult unless the concentration is sufficiently high to permit further dilution of the original sample solution.
- 1.4. The majority of the airborne particulate samples contain relatively large amounts of iron (mg range) which interfere considerably in the manganese and chromium determinations. It also interferes slightly in

the cobalt and copper analyses. For satisfactory analyses, the iron concentration of the sample must be determined, and the iron interference effects compensated for, either by preparing and using the proper interference standards or utilizing the accompanying computer program.

1.5. The accuracy obtained with this method is quite dependent upon the wet ashing procedure used for taking the trace metals into solution. When applied to the airborne particulates which have been trapped on Hi-Vol filters (fiber glass), there are a number of inherent drawbacks which include: 1) insufficient leaching of the trace metals from the relatively large amount of glass fiber filter material present, which itself is not greatly affected by the acids; 2) if the iron content of the sample is high, complete dissolution of the iron is not always accomplished, and as a result, not all of the trace metals will be dissolved; 3) the large number of manipulations and the corresponding length of time involved could introduce or result in the loss of the trace metals being determined; 4) the presence in the airborne particulate material of certain organic compounds which tend to ignite or explode during the evaporation and drying steps, resulting in possible loss of the trace metals as well as a definite safety hazard; and 5) the loss of metals by the formation of insoluble silicates during the ashing process.

1.6. WARNING: The fumes from the acids used in the wet ashing procedure are extremely corrosive; therefore, this work should be done in a well-ventilated hood. Rubber gloves and safety glasses should be worn at all times. Extreme care should be taken during the evaporation and drying steps, because it tends to ignite or explode during these stages of preparation if certain organic compounds are present in the sample. Therefore, the sample should not be left unattended during these periods. Additionally, the gases employed in the use of the atomic absorption spectrophotometer are another potential hazard, and the proper precautions should be observed when they are being used.

2. Principle of Method

2.1. The Hi-Vol filter (glass fiber) upon which the airborne particulates have been trapped is divided, and the various portions are handled and weighed according to PSM-1013a.

2.2. The airborne particulate material trapped on the portion of the Hi-Vol filter designated for trace metal analysis, is wet ashed with ultra-pure acids. The resulting ash is taken into solution and diluted to 25 ml.

2.3. This sample solution is analyzed on the atomic absorption spectrophotometer for the six specified elements and also iron. The iron concentration is needed in order to make the proper iron interference corrections for the manganese, copper, cobalt, and chromium determinations.

2.4. After determining the amount of each of the various elements on the portion of the filter which is analyzed for trace metals, a total microgram quantity of each trace metal is subsequently calculated for the entire Hi-Vol filter.

3. Apparatus and Reagents

3.1. Apparatus

3.1.1. Atomic Absorption Spectrophotometer -- Jarrell-Ash Division of Fisher Scientific Company, Model 800 or equivalent, suitably equipped with an acetylene-air flame and the proper hollow-cathode lamps (viz. cobalt, chromium, copper, manganese, nickel, zinc, and iron).

3.1.2. Electric Hot Plates --Two: 20 x 12 inches, capable of being heated to at least 500°C, available from Fisher Scientific Company, Cat. No. 11-499C or equivalent.

3.1.3. Water Deionizer --Deeminizer Model CL-5 with Deeminite mixed bed ion exchange resin (FC-10 Cartridge), available from Crystalab, Inc. or equivalent.

3.1.4. Conductivity Bridge -- Yellow Springs Instrument Company, Model 31 or equivalent.

3.1.5. Low Conductivity Cell for Use with Conductivity Bridge --dip type, with cell constant of about 0.1 reciprocal cm., available from Fisher Scientific Company, Cat. No. 9-382 or equivalent.

3.1.6. Oven --capable of being controlled at the 100°C level, Fisher Isotemp Junior Gravity Convection Model, available from Fisher Scientific Company, Cat. No. 13-244-1 or equivalent.

3.1.7. Muffle Furnace --Temco Model F-1740 or equivalent.

3.1.8. Indicating Pyrometer Controller for Muffle Furnace -- capable of regulating $\pm 20^{\circ}\text{C}$ at 600°C , available from Fisher Scientific Company, Cat. No. 10-557-13 or equivalent.

3.1.9. Steam Bath -- available from Fisher Scientific Company, Cat. No. 15-488 or equivalent.

3.1.10. Beaker Tongs -- available from Fisher Scientific Company, Cat. No. 2-620 or equivalent.

3.1.11. Glassware Per Sample -- 250-ml graduated beaker; 3-inch watch glass; 400-ml beaker; 3 1/2-inch Speedyvap (Fisher Scientific Company, Cat. No. 2-609B or equivalent); three 250-ml volumetric flasks; stirring rods; Buchner type funnel with coarse fritted disc, 60-ml capacity (Fisher Scientific Company, Cat. No. 10-358J or equivalent); one 60° angle polypropylene funnel, 35-mm I.D. (Fisher Scientific Company, Cat. No. 10-320-8A or equivalent); one 1-ml disposable pipet.

3.1.12. Miscellaneous Glassware -- assorted volumetric pipets: 1, 3, 5, 10, 15, 20, 30-ml etc.; 5-ml and 10-ml graduated pipets; assorted volumetric flasks: 25, 50, 100, 250, and 1000-ml volume; one 250-ml and one 1000-ml graduated cylinder; acid storage bottles; glass washing bottle; two 1000-ml beakers; two 150-mm watch glasses; glass trays; PYREX rod, approximately 4-mm in diameter.

3.1.13. Miscellaneous -- funnel support arm, to support four funnels (available from Fisher Scientific Company, Cat. No. 14-470 or equivalent); support stands (available from Fisher Scientific Company, Cat. No. 14-670A or equivalent); wire screens, with asbestos centers (available from Fisher Scientific Company, Cat. No. 15-590B or equivalent); plastic washing bottles, 250-ml volume; assorted sized plastic bottles; metal trays; beaker brushes; test tube brushes; rubber gloves; cotton gloves; Bernzomatic propane fuel tank with Model TXI-C torch burner unit (available from Bernzomatic Corporation), or equivalent; Glad Wrap; Kimwipes; Superwipes (available from Sorg Products); filter paper, 11-mm diameter (Schleicher & Schuell Company, No. 589 white ribbon or equivalent); linear graph paper.

3.2. Reagents

3.2.1. Deionized Water -- Prepare by passing distilled water through the Deeminizer. Allow at least 2 gallons of distilled water to drain through the Deeminizer each day before using any of the deionized water. Check it frequently by pressing the button on the Deeminizer and re

the gage. Change the ion exchange resin cartridge when the needle approaches the 1 ppm range. Since the gage on the Deeminizer is not always reliable, at least once a week check the deionized water by determining its conductance on the conductivity bridge. Continue to use the deionized water as long as the conductance reads below the 10 micromho level. When the conductance rises above this level, change the ion exchange cartridge. After changing the cartridge, allow at least 5 gallons of distilled water to drain through the Deeminizer before attempting to examine or use any of the deionized water.

3.2.2. Concentrated Nitric Acid -- 65-70%, ultra-high purity grade, available from J. T. Baker Chemical Company, Ultrex-Cat. No. 4801 or equivalent. Prior to opening, allow sufficient time for the ampoule containing the nitric acid to reach equilibrium with ambient temperature. The neck of the ampoule has been lightly scored directly above the ground glass fitting. Increase the depth of the score on one side with firm, even strokes, using a file. Light the propane torch burner and heat the tip of a PYREX rod (approximately 4 mm in diameter) until the glass is glowing a bright white. Moisten the score mark on the ampoule and immediately press the hot glass rod against the mark. The glass should crack completely, following the direction of the score marking. If not, increase the depth of the score and repeat the above procedure. After opening, the ampoule may be resealed using the special cap provided.

WARNING: Always wear proper safety equipment including safety glasses and/or face mask when working with acid.

3.2.3. 6N Hydrochloric Acid -- prepare from 30% ultra-high purity grade, available from E.M. Laboratories, Inc., Suprapur - Cat. No. 318 or equivalent. Place 91 ml of deionized water in a 250-ml graduated cylinder and slowly add 159 ml of the 30% Suprapur hydrochloric acid while swirling graduate gently. Transfer to an acid storage bottle.

3.2.4. Concentrated Hydrochloric, Nitric, and Sulfuric Acids -- ACS reagent grade, available from Fisher Scientific Company or equivalent.

3.2.5. Atomic Absorption Standard Reference Solutions -- (viz. chromium, cobalt, copper, iron, manganese, nickel, and zinc), 1000 µg/ml concentration, available from Fisher Scientific Company or equivalent.

3.2.6. Cleaning Solution for both Glassware and Plasticware --

Prepare from Alconox or equivalent, following directions on container.

3.2.7. Cleaning Solution for Glassware -- Prepare with Chromerge, available from Fisher Scientific Company or equivalent. Add contents of Chromerge bottle (25 ml) to a standard 9-lb. container of concentrated sulphuric acid. Add approximately 5 ml at a time and shake well. The precipitate which forms after mixing is normal and indicates solution is saturated. Allow this precipitate to remain, as it is a reservoir of additional chromate. WARNING: Keep container closed. Contact with combustible material may cause fire or severe burns. Avoid contact with skin and eyes.

4. Procedure

4.1. Cleaning of Glassware and Plasticware -- All the glassware and plasticware used throughout the various phases of this method must be cleaned in the following manner.

4.1.1. Wash all surfaces of each piece of glassware or plasticware thoroughly with a solution of Alconox. Rinse all surfaces well with distilled water. Where applicable, fill with distilled water, add a few drops of concentrated nitric acid, and allow to sit for at least 30 minutes. Otherwise, rinse all surfaces well with approximately 1% nitric acid. Rinse at least 3 times with distilled water. Then rinse at least 5 times with deionized water. Fill flasks with deionized water and store until ready for use. Air dry remainder of glassware. Take care not to touch any surface that is to be in contact with the sample, sample solutions, or standard reference solutions. This cleaning procedure must be strictly adhered to in order not to contaminate either the samples or standards.

4.1.2. Clean all glassware or plasticware which is to be reused in the same manner as specified in paragraph 4.1.1.

4.1.3. Place pipets in a 1000-ml graduated cylinder filled with cleaning solution (reagent 3.2.7.). Allow pipets to soak in the cleaning solution for at least one hour. Drain the cleaning solution from the pipettes back into the cylinder. Rinse the pipets outside and inside with distilled water. With an aspirator, draw deionized water from a beaker through each pipet for several minutes. Drain pipets and air dry. Use care while handling the pipets in the cleaning solution as this solution is extremely corrosive. Wear rubber gloves and safety glasses.

4.2. Division of Hi-Vol Filter to Obtain Sample of Airborne Particulates--

Divide the Hi-Vol filter (fiber glass) upon which the airborne particulates have been trapped; handle and weigh the various portions as specified in PSM-1013a (paragraph 4.2.).

4.3. Wet Ashing of Airborne Particulate Sample -- The fumes from the acids used in the wet ashing procedure are extremely corrosive; therefore, perform all the following steps in a very clean, well-ventilated hood. Wear rubber gloves and safety glasses at all times.

4.3.1. Push the folded filter containing the trapped airborne particulates down into the bottom of the 250-ml beaker, tearing the filter as little as possible. Cover the filter with 50 ml of concentrated HNO_3 (reagent 3.2.2.). Place the beaker on the 130°C hot plate; continue to heat for 30 minutes after the acid begins to simmer. Use wire screens to avoid excessive boiling. Hold the filter down in the acid with a stirring rod. Keep the beaker covered with a watch glass.

4.3.2. Place the Buchner type funnel on the support rack and the 400-ml beaker under the funnel. Label the 400-ml beaker and the funnel with the sample number. After the filter has simmered in the acid for 30 minutes, rinse the watch glass into the 400-ml beaker with deionized water from a plastic washing bottle. Decant the acid solution, while hot, through the funnel, retaining as much of the filter as possible in the beaker. Pour approximately 40 ml of hot deionized water over the filter in the beaker; then swirl the contents to rinse the filter. Decant the water rinse through the funnel, after the hot acid solution has drained through. Repeat the water rinse and decant again. Using a minimum of deionized water from a plastic washing bottle, rinse the solid material in the funnel back into the 250-ml beaker containing the filter. Rinse the bottom of the funnel into the 400-ml beaker. Mix the contents of the 400-ml beaker well by swirling, or stirring with a glass rod. When a rod is used, remove and rinse into the 400-ml beaker. Cover the 400-ml beaker with a Speedyvap watch glass, and place on a hot plate to begin evaporating the acid solution. Occasionally stir or swirl contents of the beaker as described above.

4.3.3. Repeat paragraphs 4.3.1. and 4.3.2. with 50 ml of concentrated HNO_3 .

4.3.4. Repeat paragraphs 4.3.1. and 4.3.2. twice with 50 ml of 6N HCl (reagent 3.2.3.). Rinse the filter at least three times after the last acid digestion. Then squeeze as much liquid as possible out of the filter. Discard all the material in both the funnel and the 250-ml beaker.

4.3.5. Evaporate the acid solution in the 400-ml beaker to dryness. The beakers may be placed on a steam bath overnight. Try to keep any solids from hardening on the sides of the beaker by swirling the solution or using a stirring rod and a washing bottle containing deionized water.

4.3.6. After the acid solution has gone to dryness - successively, four times, add just enough (approximately 2 ml) concentrated HNO_3 from a plastic washing bottle to wet the solid material on the bottom of the cooled beaker and heat the beaker to dryness on the 130°C hot plate. Following the fourth addition of acid, heat the beaker for approximately 30 minutes after the contents are dry.

4.3.7. Heat the beaker with two wire-asbestos screens under it on the 400°C hot plate for 2-3 hours. Remove one screen and heat at least 5 minutes. Then heat the beaker directly on the hot plate for at least 5 minutes. Be cautious during this heating process: the contents of the beaker may ignite. If this happens, immediately remove the beaker from the hot plate. If, as a result of the fire, material has deposited on the sides of the beaker and on the Speedyvap, wash down with deionized water from a plastic washing bottle and evaporate to dryness at 130°C . Take up heating process where it was left off when the fire occurred. If no material has deposited on the sides of the beaker or on the Speedyvap, continue the heating process after the fire has burned itself out.

4.3.8. Remove the beaker from the 400°C hot plate and allow to cool. Add sufficient concentrated HNO_3 to moisten the solid material on the bottom of the beaker and take to dryness on the 130°C hot plate.

4.3.9. Return the beaker to the 400°C hot plate, heating it for only 30 minutes on the two screens, at least 5 minutes on one screen, and at least 5 minutes directly on the hot plate. If the contents of the beaker ignite, follow directions given in paragraph 4.3.7.

4.3.10. Repeat paragraph 4.3.8.. Then return the beaker to the 400°C hot plate, heating it for at least 5 minutes on the two screens, at least 5 minutes on one screen, and at least 5 minutes directly on the hot plate. Perform this sequence twice. If the contents of the beaker ignite, follow directions given in paragraph 4.3.7.

4.3.11. Remove the beaker from the 400°C hot plate and allow to cool. Add just enough 6 N HCl from a plastic washing bottle to wet the solid on the bottom of the beaker. Evaporate to dryness on the 130°C hot plate. Repeat two additional times.

4.3.12. Cool the beaker. Then cover with Glad Wrap and store until ready to dissolve the ash.

4.4. Preparation of Sample Solution

4.4.1. Take the ash on the bottom of the 400-ml beaker into solution with 5-6 drops of 6N HCl and a small volume of hot deionized water. Transfer the sample solution quantitatively into a 25-ml volumetric flask and dilute to volume with deionized water.

4.4.2. Original Sample Solution -- Filter the original 25-ml sample solution through S & S No. 589 white ribbon filter paper in order to remove any extremely fine glass fibers which may have gone through the fritted disc of the Buchner funnel, but DO NOT readjust the volume of the solution in the flask. Use this original 25-ml sample solution (V_1 , paragraph 5.1.1. or 5.1.2.) to determine nickel, manganese, copper, cobalt, and chromium.

4.4.3. Diluted Sample Solution -- Using a disposable pipet, pipet 1 ml (A, paragraph 5.1.1.) of the original 25-ml solution into a 25-ml volumetric flask and dilute to volume with deionized water. Use this diluted sample solution (V_2 , paragraph 5.1.1.) to determine zinc and iron.

4.5. Determination of Zinc

4.5.1. Preparation of Zinc Standards

4.5.1.1. Using the 1000 µg/ml zinc standard reference solution, prepare stock solutions of the following concentrations: 100 µg/ml, 10 µg/ml, and 1 µg/ml.

4.5.1.1.1. Use the following equation to determine the aliquot of a particular stock solution required to make up a certain volume of the concentration to be prepared:

$$\frac{C \times V}{S} = N$$

where: C = concentration of solution to be prepared, µg/ml.

V = volume of solution to be prepared, ml.

S = concentration of stock solution, µg/ml.

N = aliquot (ml) of stock solution (S) required
to obtain desired concentration.

Example: $\frac{100 \text{ µg/ml Zn} \times 1000 \text{ ml}}{1000 \text{ µg/ml Zn}} = N$

1000 µg/ml Zn

N = 100-ml aliquot

4.5.1.1.2. Make up 1 liter of each of the specified concentrations and store in a plastic bottle. For example, to prepare the 100 µg/ml zinc stock solution, make the calculation given as an example in paragraph 4.5.1.1.1., and then, as the calculation indicates, pipet 100 ml of the 1000 µg/ml zinc standard reference solution into a 1000-ml volumetric flask and dilute to volume with deionized water.

4.5.1.2. Utilizing the various zinc stock solutions, prepare a series of zinc standards, such as the following concentrations: 0.3, 1.0, 4.5, 7.5, and 15.0 µg/ml. Prepare all single element standards as indicated in paragraphs 4.5.1.1.1. and 4.5.1.1.2., but make up in 100-ml volume. (Note: for the best analytical results, fresh standards should be prepared prior to each analysis.)

4.5.2. Zinc Parameters for Atomic Absorption Spectrophotometer

4.5.2.1. Wavelength 2139 Å

4.5.2.2. Slit Width 75 µ

4.5.2.3. Hollow-Cathode Current	5 ma
4.5.2.4. Fuel	Acetylene - 4 scfh
4.5.2.5. Oxidant	Air - 13 scfh
4.5.2.6. Burner	Laminar flow burner with 10-mm slot length.
4.5.2.7. Burner Height	9 7/16 inches
4.5.2.8. Aspiration Rate	Full
4.5.2.9. Integration Time	10 seconds
4.5.2.10. Readout Mode	Per Cent Absorption or Absorbance

4.5.3. Analysis of the Diluted Sample Solution for Zinc

4.5.3.1. Observing the proper operating instructions, including the proper safety procedure, specified in the manual for the atomic absorption spectrophotometer, set up the instrument to analyze for zinc utilizing the parameters given in paragraph 4.5.2..

4.5.3.2.1. When the instrument is operating satisfactorily, first, aspirate the standards, such as those indicated in paragraph 4.5.1.2. (Note: A series of four standards is usually sufficient; but the standards should encompass the entire analytical range of the samples being run so that at least one standard is less concentrated than the most dilute sample, and one standard is more concentrated than the most concentrated sample). Secondly, aspirate the diluted sample solution (paragraph 4.4.3.) and thirdly, aspirate the standards again.

4.5.3.2.2. For the analysis of zinc, either the per cent absorption or the absorbance readout mode may be used. If the per cent absorption readout is used, convert the per cent absorption readings to absorbance (use appropriate table in chemical handbook), and then construct a zinc working curve (Figure 1.) by plotting absorbance (use the average of the two absorbance values obtained for each standard) versus the concentrations of the various standards. Plot on linear graph paper. [Note: Absorbance is directly proportional to concentration (Beer's Law) and thus a plot of absorbance versus concentration should yield a straight line passing through the origin.] Determine the concentration value ($\mu\text{g/ml}$) for the diluted sample solution from the zinc working curve. Use this concentration value (C_2 , paragraph 5.1.1.) to calculate the total amount (micrograms) of zinc on the entire Hi-Vol filter.

4.5.3.3. If the accompanying computer program (see Appendix) is being used, aspirate four standards (paragraph 4.5.1.2.) as indicated on the computer data input sheet (the most dilute and the most concentrated standards, are aspirated once each, and the two intermediate ones are aspirated twice each - see Appendix), and record the data (either per cent absorption or absorbance) in the proper place on the computer data input sheet; then aspirate up to ten samples and record the data in the appropriate area on the computer input sheet. Utilizing these data in the accompanying program, the computer will calculate the total amount (micrograms) of zinc on the entire Hi-Vol filter.

4.6. Determination of Nickel

4.6.1. Preparation of Nickel Standards

4.6.1.1. From the 1000 µg/ml nickel standard reference solution prepare stock solutions of the following concentration: 100 µg/ml, 10 µg/ml, and 1 µg/ml. Make up 1 liter of each concentration, preparing as indicated in paragraphs 4.5.1.1.1. and 4.5.1.1.2.. Store in plastic bottles.

4.6.1.2. Using the various stock solutions, prepare a series of nickel standards of different concentrations, such as: 0.2, 0.75, 1.5, and 3.0 µg/ml. Make up 100 ml of each concentration, preparing as indicated in paragraphs 4.5.1.1.1. and 4.5.1.1.2..

4.6.2. Nickel Parameters for Atomic Absorption Spectrometer

4.6.2.1. Wavelength	2320 Å
4.6.2.2. Slit Width	150 µ
4.6.2.3. Hollow-Cathode Current	5 ma
4.6.2.4. Fuel	Acetylene - 4 1/2 scfh
4.6.2.5. Oxidant	Air 13 1/2 scfh
4.6.2.6. Burner	Laminar flow burner with 10-mm slot length
4.6.2.7. Burner Height	9 1/4 inches
4.6.2.8. Aspiration Rate	Full
4.6.2.9. Integration Time	3 seconds
4.6.2.10. Readout Mode	Concentration: with 5, 0, 0 setting on concentration dial.

4.6.3. Analysis of Original Sample Solution for Nickel

4.6.3.1. Observing the proper operating instructions, including the

proper safety procedure, specified in the manual for the atomic absorption spectrophotometer, set up the instrument to analyze for nickel employing the parameters given in paragraph 4.6.2.

4.6.3.2.1. If the accompanying computer program (see Appendix) is NOT going to be used, run the standards (paragraph 4.6.1.2.) and the original sample solution (paragraph 4.4.2.) as specified in paragraph 4.5.3.2.1..

4.6.3.2.2. For the analysis of nickel additional sensitivity is usually needed; therefore, the instrument is operated in the concentration read-out mode, the only mode in which the scale expansion feature is available. Using the arbitrary concentration readings which are obtained, construct a nickel working curve by plotting the arbitrary concentration units (use the average of the two readings obtained for each standard) versus the concentrations of the various standards. Plot on linear graph paper. Determine the concentration value ($\mu\text{g/ml}$) for the original sample solution from the nickel working curve. Use this concentration value (C_1 , paragraph 5.1.2.) to calculate the total amount (micrograms) of nickel on the entire Hi-Vol filter.

4.6.3.3. If the accompanying computer program (see Appendix) is used, run the standards (paragraph 4.6.1.2.) and the original sample solution as indicated in paragraph 4.5.3.3. Enter the arbitrary concentration readings in the proper place on the computer data input sheet, rather than per cent absorption or absorbance data. Utilizing the concentration readings in the accompanying program, the computer will calculate the total amount (micrograms) of nickel on the entire Hi-Vol filter.

4.7. Determination of Iron -- Iron interferes in the determination of manganese, copper, cobalt, and chromium. Therefore, if the accompanying computer program (see Appendix), which makes the proper iron interference corrections in the calculations for these four trace metals, is NOT going to be utilized, the concentration of the iron present in the original sample solution must be determined before these analyses are undertaken, in order that appropriate iron interference standards can be prepared and used.

4.7.1. Preparation of Iron Standards

4.7.1.1. Using the 1000 $\mu\text{g/ml}$ iron standard reference solution, prepare stock solutions of the following concentrations: 100 $\mu\text{g/ml}$, and 10 $\mu\text{g/ml}$. Make up 1 liter of each concentration, preparing as specified in paragraphs

4.5.1.1.1. and 4.5.1.1.2.. Store in plastic Bottles.

4.7.1.2. From the various stock solutions, prepare a series of iron standards, such as the following concentrations: 1.0, 2.0, 4.5, 10.0, 20.0, and 45 µg/ml. Preparing as indicated in paragraphs 4.5.1.1.1. and 4.5.1.1.2., make up 100 ml of each concentration.

4.7.2. Iron Parameters for Atomic Absorption Spectrophotometer

4.7.2.1. Wavelength	2483 Å
4.7.2.2. Slit Width	75 µ
4.7.2.3. Hollow-Cathode Current	10 ma
4.7.2.4. Fuel	Acetylene - 4 1/2 scfh
4.7.2.5. Oxidant	Air - 13 scfh
4.7.2.6. Burner	Laminar flow burner with 10-mm slot length.
4.7.2.7. Burner Height	9 1/2 inches
4.7.2.8. Aspiration Rate	Full
4.7.2.9. Integration Time	10 seconds
4.7.2.10. Readout Mode	Per cent Absorption or Absorbance

4.7.3. Analysis of the Diluted Sample Solution for Iron

4.7.3.1. Observing the proper operating instructions, including the proper safety procedure, specified in the manual for the atomic absorption spectrophotometer, set up the instrument to analyze for iron employing the parameters given in paragraph 4.7.2.

4.7.3.2. If the accompanying computer program (see Appendix) is NOT going to be used, run the standards (paragraph 4.7.1.2.) and the diluted sample solution (paragraph 4.4.3.) as specified in paragraph 4.5.3.2.1., and determine the iron concentration (µg/ml) as indicated in paragraph 4.5.3.2.2.. Use the iron concentration obtained (C_2) to calculate the concentration of iron in the original sample solution

$$\frac{C_2 \times V_2}{A} = O$$

where: O = concentration of iron in the original sample solution, µg/ml.

C_2 = concentration of iron determined in diluted sample solution, µg/ml.

V_2 = volume of diluted sample solution, ml (paragraph 4.4.3.).

A = aliquot of original sample solution used to prepare diluted sample solution, ml (paragraph 4.4.3.).

Example:

$$\frac{2 \mu\text{g/ml Fe} \times 25 \text{ ml}}{1 \text{ ml}} = O$$

O = 50 $\mu\text{g/ml Fe}$ in original sample solution

4.7.3.3. If the accompanying computer program (see Appendix) is utilized, run the standards (4.7.1.2.) and diluted sample solution as specified in paragraph 4.5.3.3.. These data will be utilized by the computer to make the proper iron interference corrections in the calculations for the manganese, copper, cobalt, and chromium determinations. (Note: The computer will also calculate the total amount of iron on the entire Hi-Vol filter.)

4.8. Determination of Manganese -- If there is iron in the original sample solution, it will interfere in the determination of manganese. The iron enhances the manganese response considerably (Figure 2.). Therefore, if the accompanying computer program (see Appendix) is NOT going to be utilized, the concentration of iron in the original sample solution must be determined before the manganese analysis is undertaken, in order that the appropriate manganese-iron interference standards can be prepared and utilized. If the accompanying computer program is used, the computer will utilize the iron data from the computer input sheet to make the proper iron interference corrections in the calculation for the manganese determination; and therefore, the iron concentration in the original sample solution need not be determined before analyzing for the manganese.

4.8.1. Preparation of Manganese Standards

4.8.1.1. Using the 1000 $\mu\text{g/ml}$ manganese standard reference solution, prepare stock solutions of the following concentration: 100 $\mu\text{g/ml}$ and 10 $\mu\text{g/ml}$. Preparing as indicated in paragraphs 4.5.1.1.1. and 4.5.1.1.2., make up 1 liter of each and store in plastic bottles.

4.8.1.2. Preparation of Manganese-Iron Interference Standards --

If the accompanying computer program is NOT being used, prepare a series of manganese-iron interference standards containing various concentrations of manganese (such as 1.0, 4.5, 7.5, and 15 $\mu\text{g/ml}$), but with each standard also containing the same concentration of iron ($\mu\text{g/ml}$) which was calculated (paragraph 4.7.3.2.) to be present in the original sample solution. Prepare 100 ml of each standard from the manganese and iron stock solutions.

4.8.1.2.1. As indicated in paragraph 4.5.1.1.1., calculate the aliquot of manganese stock solution needed to obtain a specific concentration of manganese, and also the aliquot of iron stock solution needed to match the concentration of iron in the original sample solution. (Note: The iron aliquot will be the same for the entire series, while the manganese aliquot will vary depending on the concentration being prepared.)

4.8.1.2.2. After calculating the manganese and iron aliquots required, pipet both aliquots into the same 100-ml volumetric flask and dilute to volume with deionized water. For example, to prepare a manganese-iron interference standard containing 15 µg/ml manganese and 50 µg/ml iron, pipet 15 ml of the 100 µg/ml manganese stock solution and 5 ml of the 1000 µg/ml iron standard reference solution into the same 100-ml volumetric flask, and dilute to volume with deionized water.

4.8.1.3. If the accompanying computer program is being utilized, use the manganese stock solutions to prepare a series of single element manganese standards of various concentrations, such as 1.0, 4.5, 7.5, and 15 µg/ml. Make up 100 ml of each concentration, preparing as specified in paragraphs 4.5.1.1.1. and 4.5.1.1.2..

4.8.2. Manganese Parameters for Atomic Absorption Spectrophotometer

4.8.2.1. Wavelength	2795 Å
4.8.2.2. Slit Width	75 µ
4.8.2.3. Hollow-Cathode Current	5 ma
4.8.2.4. Fuel	Acetylene - 4 scfh
4.8.2.5. Oxidant	Air - 13 scfh
4.8.2.6. Burner	Laminar flow burner with 10-mm slot length.
4.8.2.7. Burner Height	9 3/8 inches
4.8.2.8. Aspiration Rate	Full
4.8.2.9. Integration Time	3 seconds
4.8.2.10. Readout Mode	Per cent Absorption or Absorbance

4.8.3. Analysis of the Original Sample Solution for Manganese

4.8.3.1. Observing the proper operating instructions, including the proper safety procedure, specified in the manual for the atomic absorption spectrophotometer, set up the instrument to analyze for manganese employing the parameters given in paragraph 4.8.2..

4.8.3.2. If the accompanying computer program is NOT being used, run the manganese-iron interference standards (paragraph 4.8.1.2.)

original sample solution (paragraph 4.4.2.) as specified in paragraph 4.5.3.2.1., and determine the manganese concentration as indicated in paragraph 4.5.3.2.2.. Use the concentration value (C_1 , paragraph 5.1.2.) obtained to calculate the total amount (micrograms) of manganese on the entire Hi-Vol filter.

4.8.3.3. If the accompanying computer program is used, run the single element manganese standards (paragraph 4.8.1.3.) and the original sample solution (paragraph 4.4.2.) as specified in paragraph 4.5.3.3.. (Note: When the computer program is employed to do the calculations, the iron interference standards must not be used.) Utilizing the iron input data (see Appendix, data input sheet, columns 1-4), the computer will make the proper iron interference corrections when it calculates the total amount (micrograms) of manganese on the entire Hi-Vol filter.

4.9. Determination of Copper

If there is iron in the original sample solution, it will interfere in the determination of copper. The iron enhances the copper response slightly. Therefore, if the accompanying computer program (see Appendix) is NOT utilized, the concentration of iron in the original sample solution must be determined before the copper analysis is undertaken, in order that the appropriate copper-iron interference standards can be prepared and used. If the accompanying computer program is employed, the computer will utilize the iron data from the computer input sheet to make the appropriate iron interference corrections in the calculations for the copper determination; and, therefore, the iron concentration in the original sample solution need not be determined before analyzing for the copper.

4.9.1. Preparation of Copper Standards

4.9.1.1. From the 1000 $\mu\text{g/ml}$ copper standard reference solution, prepare stock solutions of the following concentrations: 100 $\mu\text{g/ml}$ and 10 $\mu\text{g/ml}$. Make up 1 liter of each, preparing as specified in paragraphs 4.5.1.1.1. and 4.5.1.1.2.. Store in plastic bottles.

4.9.1.2. Preparation of Copper-Iron Interference Standards

If the accompanying computer program is NOT being utilized, prepare a series of copper-iron interference standards containing various concentrations of copper (such as 0.5, 2.0, 4.5 and 10.0 $\mu\text{g/ml}$), but with each standard also containing the same concentration of iron ($\mu\text{g/ml}$)

which was calculated (paragraph 4.7.3.2.) to be present in the original sample solution (paragraph 4.4.2.). Preparing as specified in paragraphs 4.8.1.2.1. and 4.8.1.2.2., make up 100 ml of each standard from the copper and iron stock solutions.

4.9.1.3. If the accompanying computer program is being employed, use the copper stock solutions to prepare a series of single element copper standards, such as the following concentrations: 0.5, 2.0, 4.5, and 10.0 µg/ml. Preparing as specified in paragraphs 4.5.1.1.1. and 4.5.1.1.2., make up 100 mls of each concentration.

4.9.2. Copper Parameters for Atomic Absorption Spectrophotometer

4.9.2.1. Wavelength	3247 Å
4.9.2.2. Slit Width	75 µ
4.9.2.3. Hollow Cathode Current	5 ma
4.9.2.4. Fuel	Acetylene - 4 scfh
4.9.2.5. Oxidant	Air - 12 scfh
4.9.2.6. Burner	Laminar flow burner with 10-mm slot length.
4.9.2.7. Burner Height	9 3/8 inches
4.9.2.8. Aspiration Rate	Full
4.9.2.9. Integration Time	3 seconds
4.9.2.10. Readout Mode	Per Cent Absorption or Absorbance

4.9.3. Analysis of Original Sample Solution for Copper

4.9.3.1. Observing the proper operating instructions, including the proper safety procedure, specified in the manual for the atomic absorption spectrophotometer, set up the instrument to analyze for copper utilizing the parameters given in paragraph 4.9.2.

4.9.3.2. If the accompanying computer program is NOT being employed, run the copper-iron interference standards (paragraph 4.9.1.2.) and the original sample solution (paragraph 4.4.2.) as specified in paragraph 4.5.3.2.1., and determine the copper concentration as specified in paragraph 4.5.3.2.2. Use the concentration value (C_1 , paragraph 5.1.2.) obtained to calculate the total amount (micrograms) of copper on the entire Hi-Vol filter.

4.9.3.3. If the accompanying computer program is used, run the single element copper standards (paragraph 4.9.1.3.) and the original sample solution (paragraph 4.4.2.) as specified in paragraph 4.5.3.3.. (Note:

When the computer program is employed to do the calculations, the iron interference standards must not be used.) Utilizing the iron input data (see Appendix, data input sheet, columns 1-4), the computer will make the proper iron interference corrections when calculating the total amount (microgram) of copper on the entire Hi-Vol filter.

4.10. Determination of Cobalt

If there is iron in the original sample solution, it will interfere in the determination of cobalt. The iron enhances the cobalt response. Therefore, if the accompanying computer program (see Appendix) is NOT employed, the concentration of iron in the original sample solution must be determined before the cobalt analysis is undertaken, in order that the appropriate cobalt-iron interference standards can be prepared and used. If the accompanying computer program is employed, the computer will utilize the iron data from the computer input sheet to make the appropriate iron interference corrections in the calculations for the cobalt determination; and therefore, the iron concentration in the original sample solution need not be determined before analyzing for the cobalt.

4.10.1. Preparation of Cobalt Standards

4.10.1.1. Use the 1000 $\mu\text{g/ml}$ cobalt standard reference solution to prepare stock solutions of the following concentrations: 100 $\mu\text{g/ml}$, 10 $\mu\text{g/ml}$, and 1 $\mu\text{g/ml}$. Preparing as specified in paragraphs 4.5.1.1.1. and 4.5.1.1.2., make up 1 liter of each and store in plastic bottles.

4.10.1.2. Preparation of Cobalt-Iron Interference Standards

If the accompanying computer program is NOT being employed, prepare a series of cobalt-iron interference standards containing various concentrations of cobalt (such as 0.1, 0.3, 1.0, and 3.0 $\mu\text{g/ml}$), but with each standard also containing the same concentration of iron ($\mu\text{g/ml}$) which was calculated (paragraph 4.7.3.2.) to be present in the original sample solution (paragraph 4.4.2.). Make up 100 ml of each standard from the cobalt and iron stock solutions, preparing as specified in paragraphs 4.8.1.2.1. and 4.8.1.2.2..

4.10.1.3. If the accompanying program is being utilized, use the cobalt stock solutions to prepare a series of single element cobalt standards of various concentrations, such as 0.1, 0.3, 1.0, and 3.0 $\mu\text{g/ml}$. Preparing as specified in paragraphs 4.5.1.1.1. and 4.5.1.1.2., make up 100 ml of each concentration.

4.10.2. Cobalt Parameters for Atomic Absorption Spectrophotometer

4.10.2.1. Wavelength	2407 Å
4.10.2.2. Slit Width	75 μ
4.10.2.3. Hollow-Cathode Current	5 ma
4.10.2.4. Fuel	Acetylene - 4 scfh
4.10.2.5. Oxidant	Air - 13 scfh
4.10.2.6. Burner	Laminar flow burner with 10-mm slot length.
4.10.2.7. Burner Height	9 1/2 inches
4.10.2.8. Aspiration Rate	Full
4.10.2.9. Integration Time	3 seconds
4.10.2.10. Readout Mode	Concentration: with 5, 0, 0 setting on concentration dial.

4.10.3. Analysis of Original Sample Solution for Cobalt

4.10.3.1. Observing the proper operating instructions, including the proper safety procedure, specified in the manual for the atomic absorption spectrophotometer, set up the instrument to analyze for cobalt utilizing the parameters given in paragraph 4.10.2.

4.10.3.2. If the accompanying computer program is NOT being used, run the cobalt-iron interference standards (paragraph 4.10.1.2.) and the original sample solution (paragraph 4.4.2.) as specified in paragraph 4.5.3.2.1., and determine the cobalt concentration as specified in paragraph 4.6.3.2.2.. Use the concentration value (C_1 , paragraph 5.1.2.) obtained to calculate the total amount (micrograms) of cobalt on the entire Hi-Vol filter.

4.10.3.3. If the accompanying computer program is used, run the single element cobalt standards (paragraph 4.10.1.3.) and the original sample solution (paragraph 4.4.2.) as specified in paragraph 4.5.3.3.. (Note: When the computer program is employed to do the calculations the cobalt-iron interference standards must not be used.) Utilizing the iron input data (see Appendix, data input sheet, columns 1-4), the computer will make the proper iron interference corrections when calculating the total amount (micrograms) of cobalt on the entire Hi-Vol filter.

4.11. Determination of Chromium

If there is iron in the original sample solution it will interfere in the determination of chromium. The iron suppresses the chromium response considerably. Therefore, if the accompanying computer program

(see Appendix) is NOT utilized, the concentration of iron in the original sample solution must be determined in order that the appropriate chromium-iron interference standards can be prepared and used. If the accompanying computer program is employed, the computer will utilize the iron data from the computer input sheet to make the appropriate iron interference corrections in the calculations for the chromium determination; and therefore, the iron concentration in the original sample solution need not be determined before analyzing for the chromium.

4.11.1. Preparation of Chromium Standards

4.11.1.1. From the 1000 µg/ml chromium standard reference solution prepare stock solutions of the following concentrations: 100 µg/ml, 10 µg/ml, and 1 µg/ml. Make up 1 liter of each, preparing as specified in paragraphs 4.5.1.1.1. and 4.5.1.1.2. Store in plastic bottles.

4.11.1.2. Preparation of Chromium-Iron Interference Standards

If the accompanying computer program is NOT being utilized, prepare a series of chromium-iron interference standards containing various concentrations of chromium (such as 0.1, 0.3, 0.5, 1.5, 3.0, and 4.5 µg/ml), but with each standard also containing the same concentration of iron (µg/ml) which was calculated (paragraph 4.7.3.2.) to be present in the original sample solution (paragraph 4.4.2.). Preparing as specified in paragraphs 4.8.1.2.1. and 4.8.1.2.2., make up 100 ml of each standard from the chromium and iron stock solutions.

4.11.1.3. If the accompanying computer program is being employed, use the chromium stock solutions to prepare a series of single element chromium standards, such as the following concentrations: 0.1, 0.3, 0.5, 1.5, 3.0, and 4.5 µg/ml. Make up 100 ml of each concentration, preparing as specified in paragraphs 4.5.1.1.1. and 4.5.1.1.2.

4.11.2. Chromium Parameters for Atomic Absorption Spectrophotometer

4.11.2.1. Wavelength	3579 Å
4.11.2.2. Slit Width	150 µ
4.11.2.3. Hollow-Cathode Current	5 ma
4.11.2.4. Fuel	Acetylene- 5 3/4 scfh
4.11.2.5. Oxidant	Air - 13 1/2 scfh
4.11.2.6. Burner	Laminar flow burner with 10-mm slot length.
4.11.2.7. Burner Height	9 9/16 inches
4.11.2.8. Aspiration Rate	Full

- 4.11.2.9. Integration Time 3 seconds
4.11.2.10. Readout Mode Concentration: with 5, 0, 0 setting
on concentration dial.

4.11.3. Analysis of Original Sample Solution for Chromium

4.11.3.1. Observing the proper operating instructions, including the proper safety procedure, specified in the manual for the atomic absorption spectrophotometer, set up the instrument to analyze for chromium utilizing the parameters given in paragraph 4.11.2.

4.11.3.2. If the accompanying computer program is NOT being employed, run the chromium-iron interference standards (paragraph 4.11.1.2.) and the original sample solution (paragraph 4.4.2.) as specified in paragraphs 4.5.3.2.1., and determine the chromium concentration as specified in paragraph 4.6.3.2.2.. Use the concentration value (C_1 , paragraph 5.1.2.) obtained to calculate the total amount (micrograms) of chromium on the entire Hi-Vol filter.

4.11.3.3. If the accompanying computer program is used, run the single element chromium standards (paragraph 4.11.1.3.) and the original sample solution (paragraph 4.4.2.) as specified in paragraph 4.5.3.3.. (Note: When the computer program is employed to do the calculations, the iron interference standards must not be used.) Utilizing the iron input data (see Appendix, data input sheet, columns 1-4), the computer will make the proper iron interference corrections when calculating the total amount (micrograms) of chromium on the entire Hi-Vol filter.

5. Calculations

5.1. If the computer program is NOT used, calculate the results as follows:

5.1.1. Calculations for Diluted Sample Solution (Zinc and Iron)

$$\frac{E \times C_2 \times V_2 \times V_1}{P \times A} = T$$

where: T = total amount of trace metal on entire Hi-Vol filter, μg .

E = weight of entire Hi-Vol filter, g.

(PSM-1013a, paragraph 5.1.3., weight sheet-column 6).

C_2 = concentration of diluted sample solution, $\mu\text{g/ml}$.

(zinc-paragraph 4.5.3.2.2., or iron-paragraph 4.7.3.2.).

V_1 = volume of the original sample solution, ml. (paragraph 4.4.2.).

V_2 = volume of the diluted sample solution, ml (para

A = aliquot of original sample solution used to prepare
V₂, ml (paragraph 4.4.3.).

P = portion of Hi-Vol filter analyzed for trace metal, g
(PSM-1013a, paragraph 4.2.4. or 4.2.6., weight
sheet-column 3).

5.1.2. Calculations for Original Sample Solution (Nickel, Manganese,
Copper, Cobalt, and Chromium)

$$\frac{E \times C_1 \times V_1}{P} = T$$

where: T = total amount of trace metal on entire Hi-Vol filter, µg.

E = weight of entire Hi-Vol filter, g

(PSM-1013a, paragraph 5.1.3., weight sheet-column 6).

C₁ = concentration of original sample solution, µg/ml

(nickel-paragraph 4.6.3.2.2., manganese-paragraph
4.8.3.2., copper-paragraph 4.9.3.2., cobalt-paragraph
4.10.3.2., chromium-paragraph 4.11.3.2.).

V₁ = volume of original sample solution, ml (paragraph 4.4.2.).

P = portion of Hi-Vol filter analyzed for trace metal, g
(PSM-1013a, paragraph 4.2.4., or 4.2.6., weight
sheet - column 3).

5.2. Computer Program

The Appendix contains the listing of a Fortran computer program which makes the proper corrections for the interference of iron in the manganese, copper, cobalt, and chromium determinations, and also calculates the total amount of each of the six specified trace metals present on the entire Hi-Vol filter. When this program is used, single element standards only must be used.

5.2.1. Computer Data Input (see data input sheet, Appendix)

<u>Card</u>	<u>Column Number</u>	<u>Data Input</u>
1	1 - 8	Analytical number
	15 - 16	Number of samples, right justified.

<u>Card</u>	<u>Column Number</u>	<u>Data Input</u>
1	18 (Fe) 19 (Co) 20 (Cr) 21 (Cu) 22 (Mn) 23 (Ni) 24 (Zn)	Leave blank if Absorbance or Concentration mode was used. Put a 1 in appropriate column if % Absorption mode was used.
2 - 7	1 - 34	Concentrations of the various standards used for each element. If the concentration is <u>not</u> a whole number, enter the decimal point in the proper position. (Note: for each element, two of the concentrations are usually run once each, and two of them twice each.)
8 - 13	1 - 34	Mode readout (% A, Abs, or Conc.) of various standards used for each element. The computer automatically places the decimal point between the first and second digits for the % A mode.
14 - 23	1 - 34	Mode readout (% A, Abs, or Conc.) of the elements for the samples. (Note: The readout mode must be the same for both standards and samples.)
	39	Leave blank if the <u>diluted sample solution</u> was run for zinc and iron. Put in a 2 for the appropriate sample, if the <u>original sample solution</u> was run for zinc and iron.
	41 - 48	Weight of the entire Hi-Vol filter, in grams including the decimal point.
	50 - 56	Weight of the portion of the Hi-Vol filter analyzed for trace metals, in grams including the decimal point.
Card after last data set	80	Must have a 1.

6. References

- 6.1. RFP NO. EPAR 71-NEG. 118, Table I- paragraph 6.
- 6.2. Parma Technical Center Notebooks, 150- B series.
- 6.3. Parma Technical Center Notebook, No. 572-6.

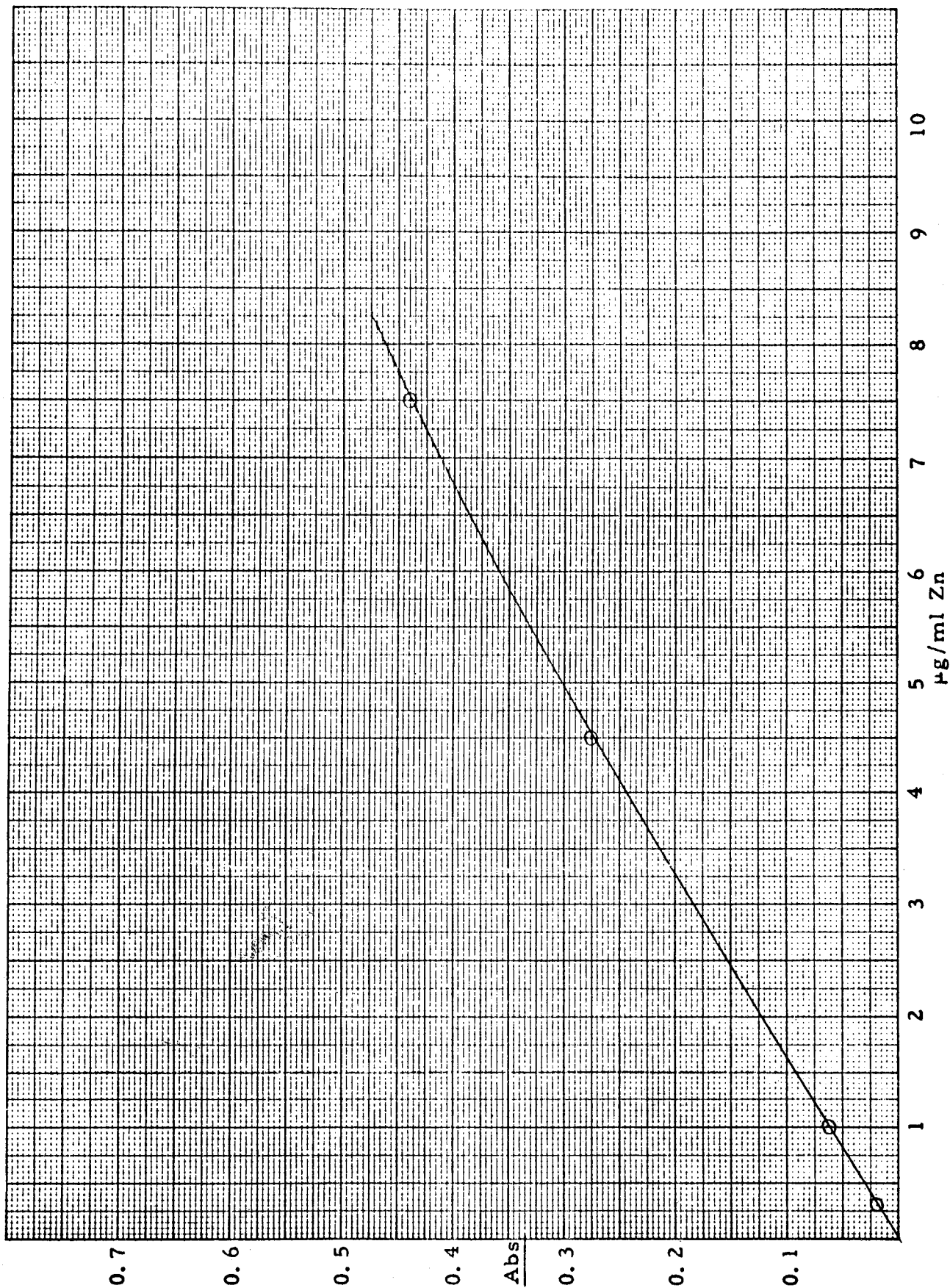


Figure 1. Zinc Working Curve

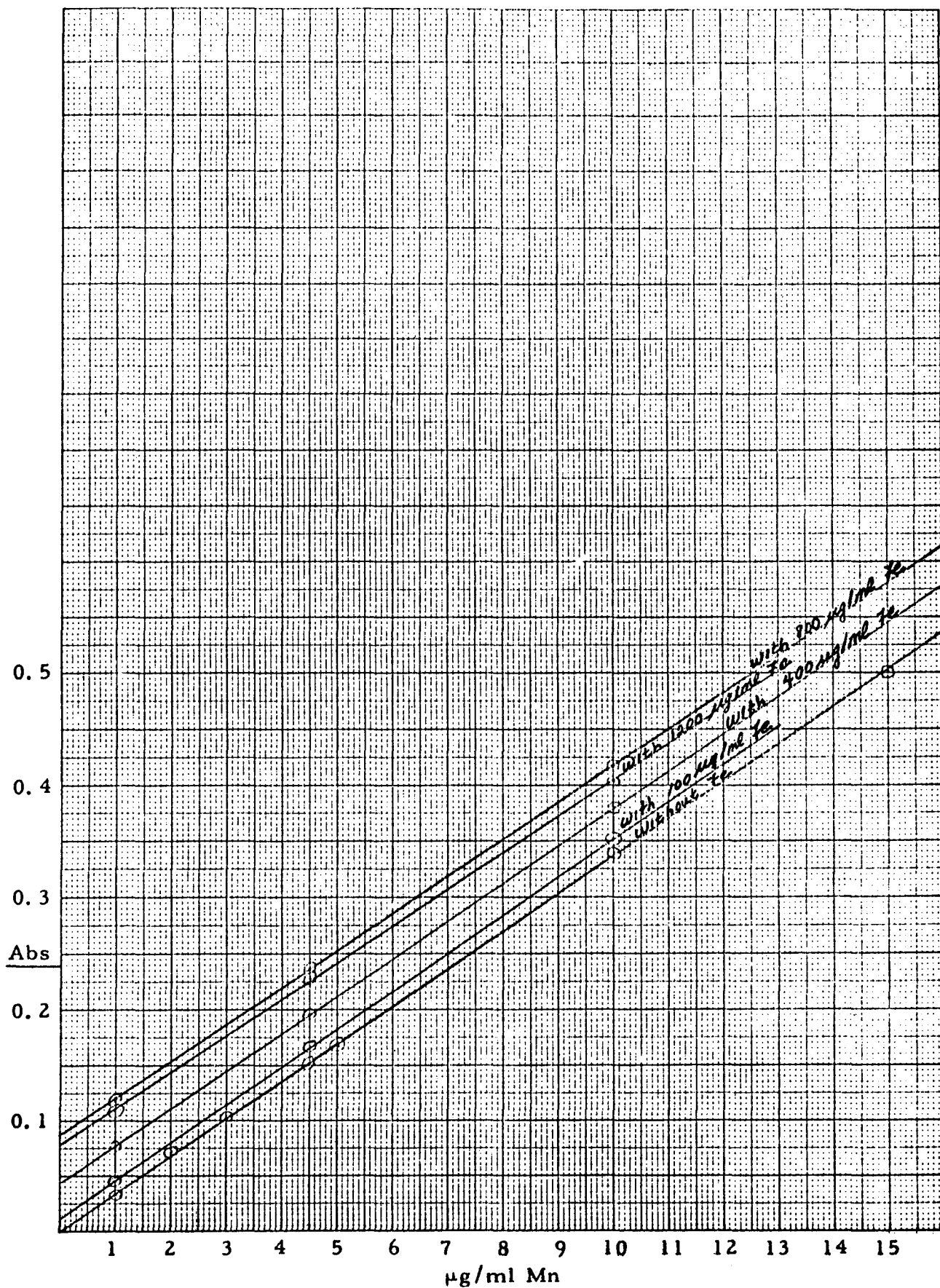


Figure 2. Manganese Working Curve and Manganese-Iron Interference Working Curves.

ATOMIC ABSORPTION DATA INPUT SHEET

1 Card

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
ANALYTICAL NUMBER																								
% or A code																								

Concentrations ($\mu\text{g/ml}$) of the Various Standards Used for Each Element

Standard

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Fe																									
Co																									
Cr																									
Cu																									
Mn																									
Ni																									
Zn																									

1
2
2
3
3
4

Mode Readout (%A, Abs, or Conc.) of Various Standards Used for Each Element

Standard

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Fe																									
Co																									
Cr																									
Cu																									
Mn																									
Ni																									
Zn																									

1
2
2
3
3
4

Mode Readout (%A, Abs, or Conc.) of the Elements for the Samples

Sample

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Fe																									
Co																									
Cr																									
Cu																									
Mn																									
Ni																									
Zn																									

Total Filter Weight

Sample Weight

1
2
3
4
5
6
7
8
9
10

APPENDIX

FORTRAN Computer Program for Trace Metal Analyses

(Makes the proper corrections for the interference of iron in the Mn, Cu, Co, and Cr determinations and also calculates the amount of each of the six specified trace metals trapped on the entire Hi-Vol filter.)

```

// JOB
// FOR AACAL
*IDCS(1443 PRINTER,CARD)
**ATOMIC ABSORPTION CALCULATIONS
*(ONE WORD INTEGERS
*NUNPROCESS PROGRAM
*LIST ALL
  DIMENSION ICONV(8),IANAL(4),A(8),STDCN(8,6),STDDT(8,6),COFA(8)
  1,COFB(8),COFC(8)
  10 READ(2,1001)IANAL,NS,ICONV,ILAST
  1001 FORMAT(4A2,6X,I2,1X,8I1,54X,I1)
  IF(ILAST)50,50,999
  50 READ(2,1002)STDCN,STDDT
  1002 FORMAT(F4.0,7F5.0)
  WRITE(3,1005)IANAL
  1005 FORMAT('ANALYTICAL NUMBER ',4A2///16X,'FE',8X,'CO',8X,'CR',8X,'CU
  1',8X,'MN',8X,'NI',8X,'ZN'/)
  GO 100 I=1,7
  IF(ICONV(I))100,100,110
  110 DO 120 J=1,6
  120 STDDT(I,J)=-.4343*ALOG(1.0-STDDT(I,J)/1000.0)
  100 CONTINUE
  DO 130 I=1,7
  SX=0.0
  SX2=0.0
  SX3=0.0
  SX4=0.0
  SY=0.0
  SXY=0.0
  SX2Y=0.0
  DO 140 J=1,6
  X=STDDT(I,J)
  Y=STDCN(I,J)
  SX=SX+X
  SX2=SX2+X*X
  SX3=SX3+X*X*X
  SX4=SX4+X*X*X
  SY=SY+Y
  SXY=SXY+X*Y
  140 SX2Y=SX2Y+X*X*Y
  ZB=SX/6.0-SX2/SX
  ZC=SX2/6.0-SX3/SX
  ZP=SY/6.0-SXY/SX
  WB=SX/6.0-SX3/SX2
  WC=SX2/6.0-SX4/SX2
  WP=SY/6.0-SX2Y/SX2
  COFA(I)=(WP-WB*ZP/ZB)/(WC-WB*ZC/ZB)
  COFB(I)=ZP/ZB-(ZC/ZB)*COFA(I)
  130 COFC(I)=(SY-SX*COFB(I)-SX2*COFA(I))/6.0
  DO 170 J=1,NS
  READ(2,1003)A,TFW,SW
  1003 FORMAT(F4.0,7F5.0,1X,F8.0,1X,F7.0)
  SWFAC=TFW/SW
  DO 150 I=1,7
  C=A(I)
  IF(ICONV(I))150,150,160
  160 C=-.4343*ALOG(1.0-C/1000.0)
  150 A(I)=COFA(I)*C+C*COFB(I)*C+COFC(I)
  IF(A(8)-2)200,210,200
  200 A(1)=A(1)*25.0
  A(7)=A(7)*25.0
  210 Z=A(1)
  X=A(5)

  A(5)=-4.875+1.031*X+.01109*Z+5.089E-6*Z*Z+2.680*.4343*ALOG(Z)
  X=A(4)
  A(4)=-.125+1.023*X+.000342*Z-5.0E-7*Z*Z-.0854*.4343*ALOG(Z)
  X=A(2)
  A(2)=+.604+.9514*X+.000259*Z-5.0E-7*Z*Z-.3428*.4343*ALOG(Z)
  X=A(3)
  A(3)=+.0970+2.017*X-.000607*X*Z

  DO 180 I=1,7
  A(I)=A(I)*25.0*SWFAC
  IF(A(I))190,180,180
  190 A(I)=0.0
  180 CONTINUE
  170 WRITE(3,1004)(A(I),I=1,7)
  1004 FORMAT(11X,8F10.1)
  GO TO 10
  999 CALL EXIT
  END
// XEO AACAL
*CCEND

```

PARMA STANDARD TEST METHODS
UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM- 1015	ANALYSIS Benzene, Toluene, Xylene & Naphthalene
RANGE 0 to 700 µg each of all components	KEY REAGENT Gas Chromatograph
PRECISION Not determined Estimated at ± 10% at all ranges	MATRIX Charcoal containing adsorbed hydrocarbons
DATE ISSUED 12/8/71	DATE REVISED 6/2/72 8 700001

**GAS CHROMATOGRAPHIC DETERMINATION OF BENZENE,
TOLUENE, XYLENE, AND NAPHTHALENE
ADSORBED ON CHARCOAL**

1. Purpose and Limitation

- 1.1. Benzene, toluene, xylene, and naphthalene vapors which were adsorbed on charcoal are determined by gas chromatography.
- 1.2. Other volatile components which have the same gas chromatographic retention times will interfere and give high results.

2. Principle of Method

- 2.1. The charcoal is placed in a specified volume of carbon disulfide and the compounds are desorbed from the charcoal into the solvent.
- 2.2. This solution is subsequently injected into the chromatograph and the recorded areas under the benzene, toluene, xylene, and naphthalene peaks are measured.
- 2.3. The amount of benzene, toluene, xylene, and naphthalene adsorbed on the charcoal is determined by means of a calibration curve, obtained from analyzing standard solutions of the above four compounds on the gas chromatograph.

3. Apparatus, Reagents, and Gas Chromatographic Column

3.1. Apparatus

- 3.1.1. Gas Chromatograph - F & M Model 810 or equivalent equipped with a flame ionization detector.
- 3.1.2. Recorder - 1 mv. sensitivity, Texas Instruments or equivalent.
- 3.1.3. Integrator - Hewlett Packard Model 3370A or equivalent.

3.1.4. Tubing - Stainless steel, 1/8 inch O.D., 20 foot length, 0.02 inch wall thickness.

3.1.5. Swage Connectors - Four 1/8 inch nuts with ferrules.

3.1.6. Hot Plate

3.1.7. Glassware - three 100-ml volumetric flasks; one 10 μ l and one 25- μ l Hamilton syringe; one large glass evaporating tray, 6 inches by 12 inches; 4.0 ml capacity (one dram) glass vials, two for each sample; one 250-ml beaker.

3.1.8. Miscellaneous - Glass file for cutting glass tubing, spatula, glass wool.

3.1.9. Analytical Balance - Single pan type, 0.1 mg sensitivity.

3.2. Reagents

3.2.1. Chloroform, methylene chloride, benzene, toluene, m-xylene, o-xylene, naphthalene, carbon disulfide - all reagent grade.

3.2.2. Silicone Gum Rubber-SE-30 available from gas chromatographic suppliers; e.g., Analabs, Inc.

3.2.3. Chromosorb G, AW, DMCS Treated, 80-100 Mesh - available from gas chromatographic suppliers; e.g., Analabs, Inc.

3.3. Gas Chromatographic Column - 10 ft x 1/8 inch O.D. stainless steel tubing packed with 8% by weight SE-30 on Chromosorb G, AW, DMCS Treated, 80-100 mesh.

3.3.1. Column Preparation - Add 8.0 grams of SE-30 to a 250-ml beaker. Dissolve in 100 ml of chloroform and 100 ml of methylene chloride. Add this solution to 100 grams of the Chromosorb G, AW, DMCS treated which has been spread out in the glass evaporating tray. Allow the solvent to evaporate in a hood. Occasionally, stir gently with a spatula. Apply gentle heat (about 40°C) with a hot plate to remove last traces of the solvents. Store the coated support in a clean bottle.

3.3.2. Column Packing - Cut the stainless steel tubing into two 10.0 ft lengths. Clean the inside of the tubing with acetone to remove any oil deposits. Completely dry the tubing by passing forced air through the tubing. Cap one end of each column with an end cap. With the aid of a funnel slowly pour the coated support (paragraph 3.3.1.) into the stainless steel tubing. While adding the support, vibrate the column gently by tapping to obtain a uniform packing. When the column is completely filled, remove approximately 1/4 inch of support from each end (one at

a time) and completely fill these voids with glass wool. Firmly attach a Swage nut and ferrules to each end of each column. Coil the columns so they will fit into the oven section of the chromatograph.

3.3.3. Column Conditioning - If the instrument is equipped with a thermal conductivity (TC) detector turn off the current to the TC detector. (Keeping the current on when no helium is flowing through the detectors will burn out the TC detectors.) Place both columns into the oven, connecting the front end of the column to the injection port (or equivalent position). Do not connect the end of the column to the detector inlet. Bake the columns at 250°C overnight with a low helium flow (Approximately 20 cc/min.). Connect the columns to the detector inlet after the overnight bake.

4. Procedure

4.1. Gas Chromatographic Parameters (F & M 810)

4.1.1. Column Temperature - 60°C for three minutes, then program to 210°C at 20°C/min. Hold at 210°C for 6 minutes.

4.1.2. Detector Temperature - 300°C

4.1.3. Injection Port Temperature - 280°C

4.1.4. Carrier Gas - helium

4.1.5. Carrier Gas Flow - 40 cc/min. In order to obtain high sensitivity, all helium flow should pass through the flame ionization detector.

4.1.6. Hydrogen Flow - about 60 cc/min. (50 psi).

4.1.7. Air Flow - about 400 cc/min. (50 psi).

4.1.8. Sample Injection Volume - 5 μ l

4.1.9. Approximate Retention Times

<u>Compound</u>	<u>Retention Times (sec.)</u>
benzene	295
toluene	413
m-xylene	503
p-xylene	503
o-xylene	523
naphthalene	734

4.1.10. Total Elution Time - 20 minutes

4.2. Integrator Parameters (Hewlett Packard 3370A)

4.2.1. Noise Suppression - 3

4.2.2. Up Slope Sensitivity - 0.1

4.2.3. Down Slope Sensitivity - 0.03

4.2.4. Baseline Delay - 0.05

4.2.5. Front Shoulder - ON

4.2.6. Rear Shoulder - 1

4.2.7. Peak Summation - 1000

4.3. Preparation of Calibration Graph

4.3.1. To the nearest 0.1 mg, weigh approximately 5, 10, and 25 mg of naphthalene and add to three 100-ml volumetric flasks. Fill each volumetric flask about half full with carbon disulfide.

4.3.2. To the flask containing approximately 5.0 mg of naphthalene, add (using a Hamilton syringe) 5.0 μl each of benzene, toluene, m-xylene, and o-xylene. To the flask containing approximately 10.0 mg of naphthalene add 10.0 μl each of benzene, toluene, m-xylene, and o-xylene. To the flask containing approximately 25.0 mg of naphthalene add 25.0 μl each of benzene, toluene, m-xylene, and o-xylene.

4.3.3. Dilute the three flasks to volume with carbon disulfide and mix well.

4.3.4. Using the above gas chromatographic and integrator parameters, inject, by means of the solvent flush technique (paragraph 4.3.5.), exactly 5.0 μl of each standard. Run each standard three times and obtain the area (integrator counts) under each of the following peaks: benzene, toluene, m-xylene, o-xylene, and naphthalene. For each standard, calculate the average integrator counts of benzene, toluene, m-xylene, o-xylene, and naphthalene obtained from the three injections.

4.3.5. Solvent Flush Injection Technique - Solvent flush technique eliminates difficulties arising from blowback or distillation within the needle of the injection syringe. First flush the 10 μl syringe with carbon disulfide several times to wet the barrel and plunger. Draw three microliters of carbon disulfide into the syringe. Remove the needle from the carbon disulfide and pull the plunger back about 0.5 μl to separate the solvent flush from the sample with a pocket of air. Immerse the needle in the sample, and withdraw the 5.0 μl aliquot. After the needle is removed from the sample, and prior to injection, pull back the plunger to minimize evaporation of the sample from the tip of the needle.

4.3.6. Use the computer program listed in appendix or plot on linear graph paper the $\mu\text{g/ml}$ of each compound in the three standards versus the

average integrator counts, (paragraph 4.3.4.). Use the following Table to obtain the $\mu\text{g/ml}$ of benzene, toluene, m-xylene, and o-xylene in each standard.

TABLE

$\mu\text{g/ml}$ of benzene, toluene, m-xylene, o-xylene in Standards

<u>Standard</u>	<u>$\mu\text{g/ml}$</u>
5.0 μl / 100 ml	43.9 - benzene
	43.3 - toluene
	43.4 - m-xylene
	44.8 - o-xylene
10.0 μl / 100 ml	87.8 - benzene
	86.7 - toluene
	86.8 - m-xylene
	89.7 - o-xylene
25.0 μl / 100 ml	219.6 - benzene
	216.7 - toluene
	216.1 - m-xylene
	224.2 - o-xylene

Use the following formula to calculate $\mu\text{g/ml}$ of naphthalene in the three standards

$$A \times 10 = B$$

where A = weight of naphthalene in milligrams to the nearest 0.1 mg, (paragraph 4.3.1.).

B = $\mu\text{g/ml}$ of naphthalene

(The factor, 10, converts mg to μg and takes into account the dilution of the standard.)

4.3.7. Caution - Once the calibration mixtures have been run on the chromatograph, do not make any adjustments to the helium, air, or hydrogen flow rates. Small changes in the flows will alter the flame ionization detector's response for each compound. If the flow has been altered, rerun the three standard calibration mixtures. If the standards are more than two days old, make up new standards.

4.3.8. A chromatogram of a calibration synthetic is indicated in Figure 1. (p-xylene elutes simultaneously with m-xylene. The detector response for m-xylene and p-xylene are very similar.)

4.4. Sample Analysis

4.4.1. Sample Tube Description - The charcoal filled glass tubes are approximately 6 cm long by 0.5 cm in diameter and are packed with two sections of 20/40 mesh activated charcoal. The "A" side contains about 2 cm of activated charcoal and was the side farthest from the pump when the sample was taken (it should contain most of the volatiles); the "B" side contains about 1 cm of activated charcoal and was the side nearest the pump. The two sections were separated with a plug of fiberglass and retained with plugs of fiberglass at each end.

4.4.2. The "A" side of the charcoal glass tube is broken as follows. Etch the "A" side tip with a file. Place a piece of 6-inch long by 1/4 inch outside diameter stainless steel tubing over the etched end and apply pressure to break the glass at the etch mark. Use care.

4.4.3. Remove the fiberglass plug on the "A" side with a small wire. Pour the charcoal from the "A" side into a one dram vial.

4.4.4. With a small wire, remove the fiberglass plug, which separates the two sections, and add the charcoal contents of the "B" side to another one dram vial.

4.4.5. With a hypodermic syringe, add 1.00 ml of carbon disulfide to each vial. Allow the adsorbed components to desorb for about 2 hours. Keep the cap tight during this period. Occasionally swirl the contents of the vial gently to mix the desorbed components. Do not allow the activated charcoal to adhere to the walls of the vial.

4.4.6. Chromatograph the contents of each vial ("A" and "B" side) three times using the above gas chromatographic parameters (paragraph 4.1.), integrator parameters (paragraph 4.2.) and the solvent flush technique (paragraph 4.3.5.).

4.4.7. Obtain the integrator counts for benzene, toluene, m-p-xylene, o-xylene, and naphthalene for each injection.

4.4.8. A typical chromatogram of a sample ("A" side) is indicated in Figure 2.

4.5. Blank Charcoal Filled Glass Tubes

4.5.1. Unused or unopened charcoal filled glass tubes may contain small amounts of benzene, toluene, m-p-xylene, o-xylene, and naphthalen

The amounts of these compounds in unopened charcoal filled glass tubes are determined in the same manner as the samples (paragraph 4.4.2.) through 4.4.6.). The average blank values are subsequently subtracted from the sample values.

5. Calculations, either use the computer program given in the appendix or do the following:

5.1. Calibration Graph

5.1.1. For each sample calculate the average integrator counts of benzene, toluene, m-p-xylene, o-xylene, and naphthalene obtained from the three "A" side injections and from the three "B" side injections (paragraph 4.4.6.).

5.1.2. For the blanks calculate the average integrator counts of benzene, toluene, m-p-xylene, o-xylene, and naphthalene obtained from the three "A" side injections and from the three "B" side injections (if more than one blank is run, average the integrator counts of each component from all blanks).

5.1.3. From the standard calibration curve (paragraph 4.3.6.) determine the $\mu\text{g/ml}$ of benzene, toluene, m-p-xylene, o-xylene, and naphthalene present in the sample's "A" side and "B" side. Use the average sample integrator count of each component (paragraph 5.1.1.) for this calculation.

5.1.4. From the standard calibration curve (paragraph 4.3.6.) determine the $\mu\text{g/ml}$ of benzene, toluene, m-p-xylene, o-xylene, and naphthalene present in the blank's "A" side and "B" side. Use the average blank integrator count of each component (paragraph 5.1.2.) for this calculation.

5.1.5. Subtract the $\mu\text{g/ml}$ of benzene, toluene, m-p-xylene, o-xylene, and naphthalene present in the blank's "A" side and "B" side, respectively, (paragraph 5.1.4.) from the $\mu\text{g/ml}$ of benzene, toluene, m-p-xylene, o-xylene, and naphthalene (paragraph 5.1.3.) in the sample's "A" side and "B" side. List and report the corrected "A" side and "B" side results from each sample.

5.2. Computer Program

The Appendix lists a FORTRAN computer program which can be used for the above calculations.

5.2.1. FORTRAN Data Input Specifications

5.2.1.1. Calibration Curve

<u>Column Number</u>	<u>Data Input</u>
1	write "1" for all calibration data
2 - 8	benzene concentration, $\mu\text{g/ml}$
9 - 16	benzene integrator counts
17 - 24	toluene concentration, $\mu\text{g/ml}$
25 - 32	toluene integrator counts
33 - 40	m-xylene concentration, $\mu\text{g/ml}$
41 - 48	m-xylene integrator counts
49 - 56	o-xylene concentration, $\mu\text{g/ml}$
57 - 64	o-xylene integrator counts
65 - 72	naphthalene concentration, $\mu\text{g/ml}$
73 - 80	naphthalene integrator counts

5.2.1.2. Samples

<u>Column Number</u>	<u>Data Input</u>
1	write "3" for no correction for blank write "4" for "A" side write "5" for "B" side
2 - 5	run number - give each "A" side and "B" side for every sample a different number, i.e., "1,2,3,4----"
7 - 16	Union Carbide Sample No.
17 - 32	Government Sample No.
33 - 40	benzene integrator counts
41 - 48	toluene integrator counts
49 - 56	m-p-xylene integrator counts
57 - 64	o-xylene integrator counts
65 - 72	naphthalene integrator counts

5.2.1.3. Miscellaneous - Calibration data and sample data must be run at the same time. All calibration data is run first. After last calibration data, place a card with a "2" in column number 1. Follow with sample data to be calculated. After last sample data card, place a card with a "2" in column number 1. The blank corrections in the computer program can be varied by changing the constants as indicated in the program listing.

6. References

- 6.1. Am. Ind. Hyg. Assoc. J., 31, 225 (1970).
- 6.2. Notebook reference 572-1.



APPENDIX

FORTRAN Computer Program for the calculation of benzene, toluene, xylene, and naphthalene adsorbed on charcoal.

```
// JCI
// FOR AL700
*IOCS(CARD,1443 PRINTER)
**GC CALCULATIONS FOR GOVERNMENT CONTRACT
*ONE WORD INTEGERS
*LIST ALL
*NONPROCESS PROGRAM
REAL M(5)
INTEGER RUN ,RUNH
DIMENSION X(5),Y(5),B(5),SUMX(5),SUMX2(5),SUMXY(5),SUMY(5),FN(5)
DIMENSION ID(13)
DO 10 I=1,5
SUMX(I)=0
SUMX2(I)=0
SUMXY(I)=0
SUMY(I)=0
10 FN(I)=0
RUNH=-1
N=0
100 READ(2,1000)J,(Y(I),X(I),I=1,5)
IF(J-1)100,110,300
110 DO 200 I=1,5
IF(Y(I))200,200,120
120 SUMX(I)=SUMX(I)+X(I)
SUMX2(I)=SUMX2(I)+X(I)**2
SUMY(I)=SUMY(I)+Y(I)
SUMXY(I)=SUMXY(I)+Y(I)*X(I)
FN(I)=FN(I)+1
200 CONTINUE
GO TO 100
300 DO 350 I=1,5
M(I)=(FN(I)*SUMXY(I)-SUMY(I)*SUMX(I))/(FN(I)*SUMX2(I)-SUMX(I)**2)
B(I)=(SUMY(I)-M(I)*SUMX(I))/FN(I)
DO 360 I=1,5
360 SUMX(I)=0
LINE=2
WRITE(3,1004)
400 READ(2,1001)J,RUN,ID,X
IF(J-2)400,450,410
410 DO 420 I=1,5
Y(I)=M(I)*X(I)
420 IF(Y(I))430,420,420
430 Y(I)=0
420 CONTINUE
IF(J-4)740,422,425
C
*** BLANK CORRECTIONS FOR SIDE A ***
422 Y(2)=Y(2)-10.1
Y(3)=Y(3)-1.9
GO TO 700
C
*** BLANK CORRECTIONS FOR SIDE B ***
425 Y(2)=Y(2)-5.0
Y(3)=Y(3)-0.3
700 IF(Y(2))710,720,720
710 Y(2)=0.0
720 IF(Y(3))730,740,740
730 Y(3)=0.0
740 IF(RUNH)485,440,440
440 IF(RUN-RUNH)450,500,450
450 DO 460 I=1,5
SUMX2(I)=SUMX(I)/N
SUMX(I)=0
XYL=SUMX2(3)+SUMX2(4)
WRITE(3,1002)SUMX2(1),SUMX2(2),XYL,SUMX2(5),SUMX2(4),SUMX2(3)
LINE=LINE+2
IF(LINE-45)480,480,470
470 WRITE(3,1004)
LINE=2
480 N=0
485 RUNH=RUN
IF(J-2)500,600,500
500 XYL=Y(3)+Y(4)
WRITE(3,1003)RUN,ID,Y(1),Y(2),XYL,Y(5),Y(4),Y(3)
LINE=LINE+1
IF(LINE-50)530,520,520
520 WRITE(3,1004)
LINE=2
530 DO 510 I=1,5
SUMX(I)=SUMX(I)+Y(I)
N=N+1
GO TO 400
1000 FORMAT(11,F7.0,9F8.0)
1001 FORMAT(11,I4,1X,12A2,5F8.0)
1002 FORMAT(11X,'***',27X,'AVERAGE',3X,6F10.1)
1003 FORMAT(1X,18,2X,5A2,10X,8A2,4X,6F10.1)
1004 FORMAT('1',10X,'UCC NUMBER',10X,'GOVERNMENT NUMBER',6X,'BENZENE T
10LUENE XYLENE NAPHTHALENE O-XYLENE MP-XYLENE')
600 CALL EXIT
END
```

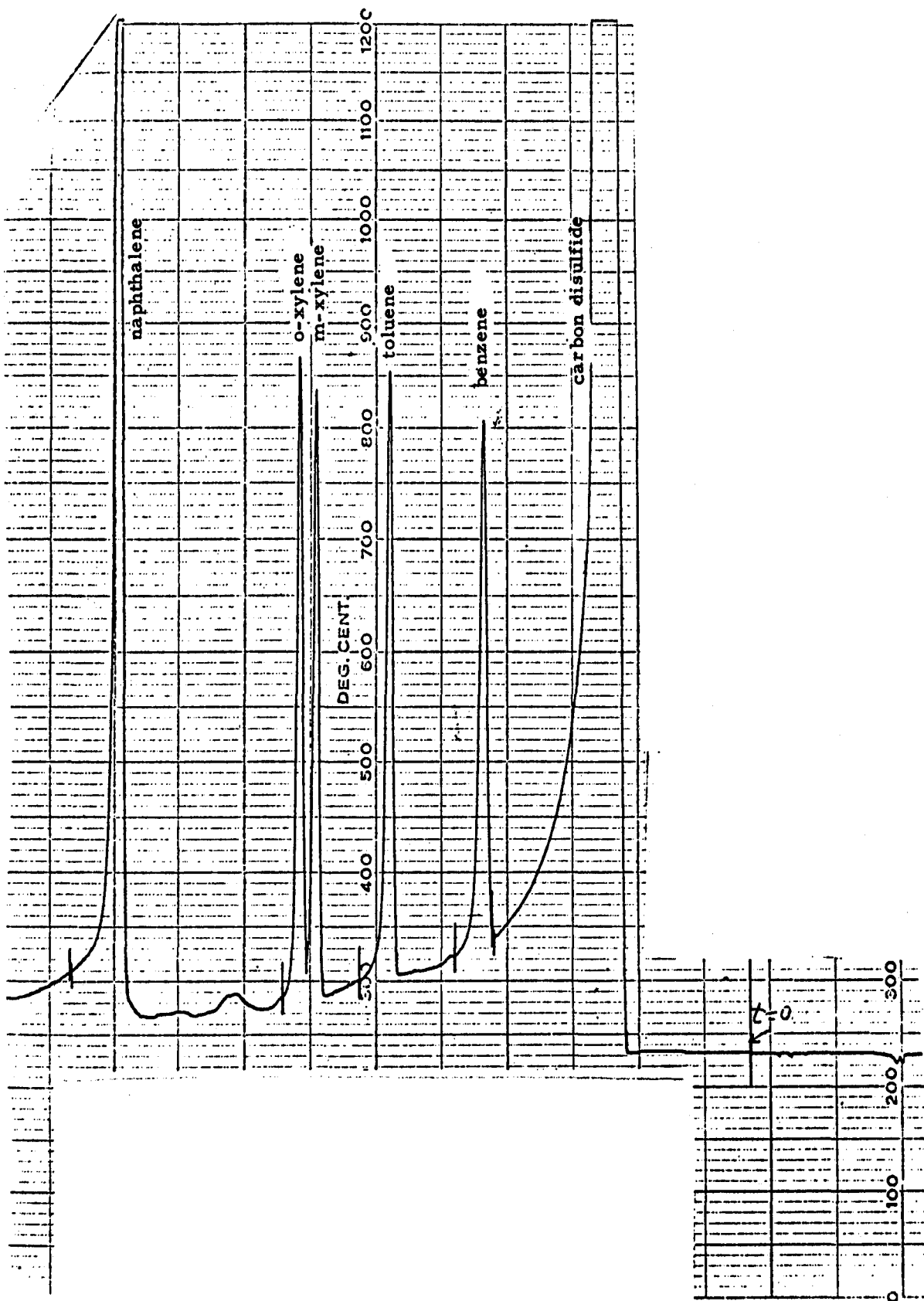



Figure 1. Chromatogram of Aromatic Synthetic (see paragraphs 4.1. and 3.3. for GC Parameters).

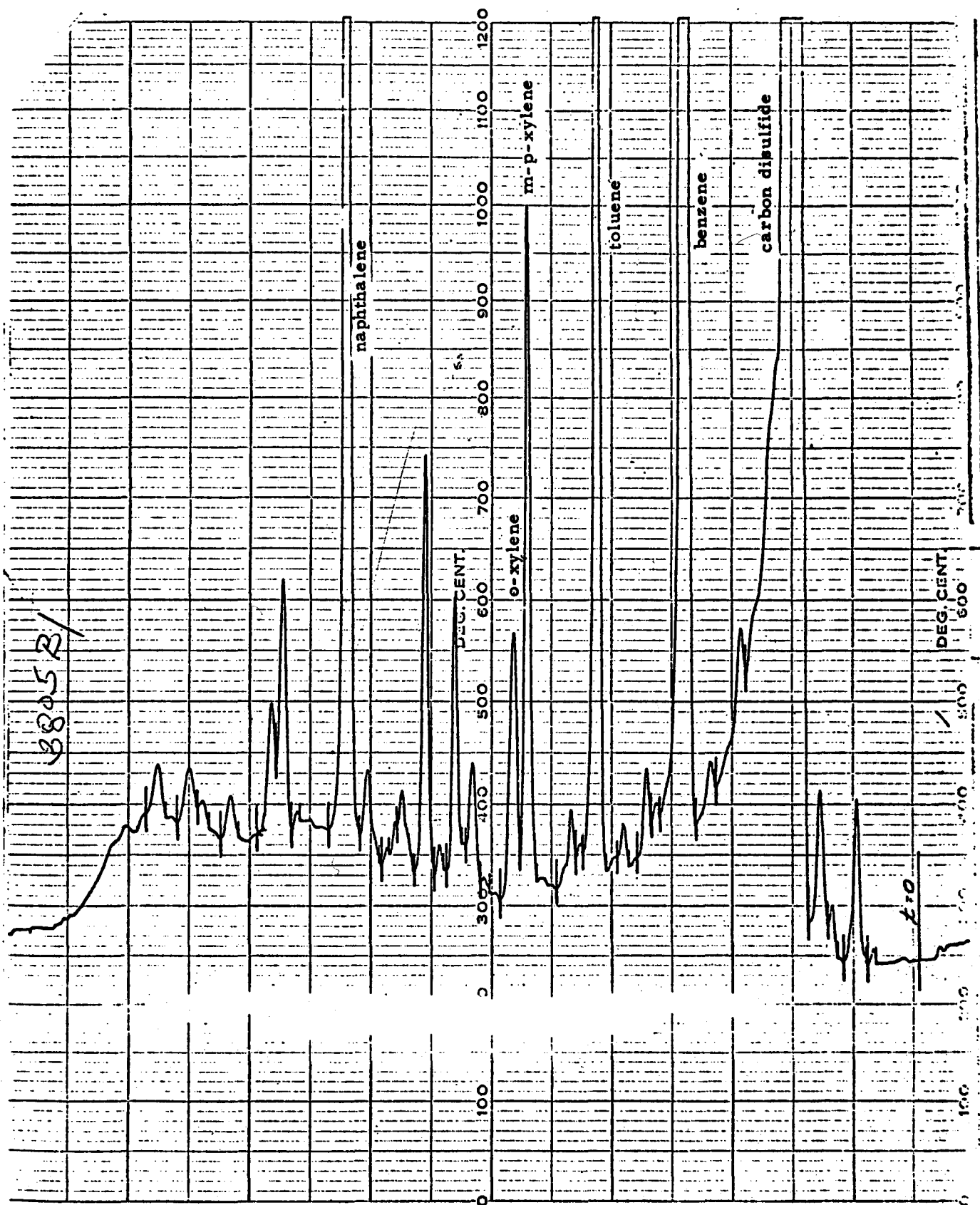


Figure 2. Chromatogram of Government Sample No. 3805A
(see paragraphs 4.1 and 3.3. for GC Parameters).

PARMA STANDARD TEST METHODS
UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM- 1018	ANALYSIS Purification by Liquid Chromatography
RANGE Not Applicable	KEY REAGENT Chromatographic Grade Alumina or other column material
PRECISION Not Applicable	MATRIX Not Applicable
DATE ISSUED 6/23/72	DATE REVISED 6 700001

PURIFICATION AND SEPARATION BY LIQUID CHROMATOGRAPHY
TO PRODUCE ULTRAPURE COMPOUNDS

1. Purpose and Limitations

1.1. This method is designed to separate impurities (organic and/or inorganic) from and purify certain compounds. The compound to be purified can be either organic or inorganic.

1.2. The limitations are associated with the large eluting solvent requirements, and the need for judgement on the part of an experienced operator to determine when one compound has been eluted and another begins.

2. Principle of Method

2.1. The mixture to be purified, either a finely ground solid or a solid dissolved in a minimum amount of solvent, is placed on a column of chromatographic grade alumina. The various compounds in the mixture are eluted at different times depending upon the different solvent polarities. Mixtures are separated into pure compounds by eluting with different solvents. The solvents used are n-heptane, benzene, chloroform, ethyl alcohol, and deionized water. The eluted compounds are identified by a variety of techniques.

3. Apparatus and Reagents

3.1. Apparatus

3.1.1. Column - eighteen inches long PYREX glass of 8-mm I.D., equipped with a Teflon stopcock at the bottom and a 500-ml reservoir sealed to the top. (Figure 1.)

- 3.1.2. Ring Stand - equipped with a buret clamp to hold the column.
- 3.1.3. Glassware - bottles, wide-mouth, 2-oz. capacity, to catch the eluate; 50-ml graduated beaker; glass rod, 2-foot long; funnel, long stem; glass bottle, 1-liter screw cap, four or more.
- 3.1.4. Water Deionized - mixed bed ion exchanger for purifying water (Deeminize Model CL-5 with FC-10 Cartridge).
- 3.1.5. Infrared Spectrophotometer - Perkin-Elmer Model 221 or equivalent.
- 3.1.6. Mortar and Pestle - Agate
- 3.1.7. Ultraviolet Lamp - long wavelength, tube type from General Electric Corporation or equivalent.
- 3.1.8. Aluminum Foil - household type
- 3.2. Reagents
 - 3.2.1. Alumina - 80-200 mesh Chromatographic Grade - available from Fisher Scientific Co., Cat. No. A-540.
 - 3.2.2. PYREX Glass Wool- clean the PYREX wool by washing in chloroform, and by air drying on a watch glass. The cleaned wool is stored in a clean closed bottle.
 - 3.2.3. Benzene, chloroform and ethyl alcohol - Reagent grade.
 - 3.2.4. n-Heptane - 99 mole per cent pure.
- 4. Procedure
 - 4.1. Column Preparation
 - 4.1.1. Hold the column on a tripod support or ring stand with buret holder.
 - 4.1.2. Add a 1/2 inch plug of cleaned PYREX wool to the bottom of the column to prevent fine alumina particles from passing through the stopcock. Tamp the PYREX wool down with the glass rod.
 - 4.1.3. Use a long stem glass funnel for adding the alumina. (The stem should be long enough to prevent the alumina from scattering around in the 500-ml liquid reservoir at the top of the column.)
 - 4.1.4. Pour the alumina to the desired height. (This step should be fast enough to cut down air exposure time but slow enough not to plug the neck of the column.)
 - 4.1.5. Limit the height of the alumina to about 2 inches below the 500-ml liquid reservoir.

4.1.6. Tap the column lightly to insure proper packing, first at the stopcock, then at about the midpoint, and finally near the top. The column is properly packed when the alumina no longer settles when the column is tapped.

4.2. Preliminary cleaning and checking of solvents

4.2.1. Pour n-heptane slowly down the side of the glass reservoir through an alumina column prior to use. The column is prepared according to paragraph 4.1.

4.2.2. Purify the benzene and chloroform according to paragraph 4.2.1.

4.2.3. Use a different column for the purification of each solvent.

4.2.4. Check the purity of each solvent by evaporating approximately 150 ml of the solvent to dryness and checking the residue by infrared analysis.

4.2.5. Collect the solvent in 1-liter screw-cap bottles after verifying the purity according to paragraph 4.2.4.

4.3. Sample Preparation

4.3.1. Grind the solid sample as fine as possible in an agate mortar and transfer the ground sample to a 50-ml beaker.

4.3.2. Add approximately 30 ml of n-heptane to the powdered sample in the beaker and mix with a small spatula. (The sample is now ready to be put on the column.)

4.3.3. Pour a small amount of n-heptane onto the dry column before adding the sample. Add enough n-heptane to wet the top 3 or 4 inches of alumina leaving about 2 to 3 inches of n-heptane above the top of the alumina.

4.3.4. Quickly add the sample while the n-heptane level is still 2 to 3 inches above the alumina. (Care should be taken not to move, jar or introduce air into the column.)

(CAUTION! An n-heptane sample mixture is never added to a dry alumina column because the heat generated from the first contact with the alumina could alter the sample.)

4.3.5. Rinse the sample beaker with 30 ml of n-heptane and add the rinse to the column while the liquid level is still about 2 inches above the alumina.

4.3.6. Repeat paragraph 4.3.5. until beaker is free of sample.

4.4. Sample elution

- 4.4.1. Add approximately 200 ml of n-heptane to the column while the liquid level is still about 2 inches above the top of the alumina.
- 4.4.2. Discard the first 20-30 ml of effluents coming through the column.
- 4.4.3. Check the column for fluorescence activity with ultraviolet light, after the first few milliliters come through and use a wax pencil to mark the column where the leading edge of the sample appears.
- 4.4.4. Wrap the column with aluminum foil to prevent possible photo-oxidation of the fluorescent compounds.
- 4.4.5. Catch the effluent in 2-oz. bottles.
- 4.4.6. When the first bottle is full, check the column again with ultraviolet light and mark sample front on the column,
(CAUTION! The UV light should be used as little as possible to avoid "burning" the column nearest the light.)
- 4.4.7. Check for nonfluorescent materials by evaporating about 15 drops of the effluent collected on a watch glass. If no deposit is seen the bottle of effluent may be discarded. If a solid deposit does appear, check after each 2-oz. bottle is filled until the deposit no longer appears when the effluent is evaporated. (Do not shut the stopcock off during the first hour because air bubbles that might be present may work to the top of the column causing channeling.)
- 4.4.8. Add 50 ml of heptane-benzene mixed solvent according to Table I, when the amount of solids present in the 2-oz. bottle (paragraph 4.4.7.) has decreased or the fluorescent front stops moving. (The first solvent used is IA of Table I.)
- 4.4.9. Use solvent IA until the leading edge slowdown occurs, then use solvent IB.
- 4.4.10. Keep increasing the amount of benzene and decreasing the amount of n-heptane according to Table I until pure benzene is used.
- 4.4.11. Continue using Table II until pure chloroform is used.
- 4.4.12. Continue the elution using Table III until pure ethyl alcohol is used.
- 4.4.13. Continue the elution using Table IV as shown.
- 4.4.14. Evaporate the solvents from the bottles in a hood and collect the purified compounds.

4.4, 15. Verification of the purity of the compound can be ascertained by a variety of analytical techniques; infrared and ultraviolet spectroscopy, nuclear magnetic resonance, mass spectroscopy and others.

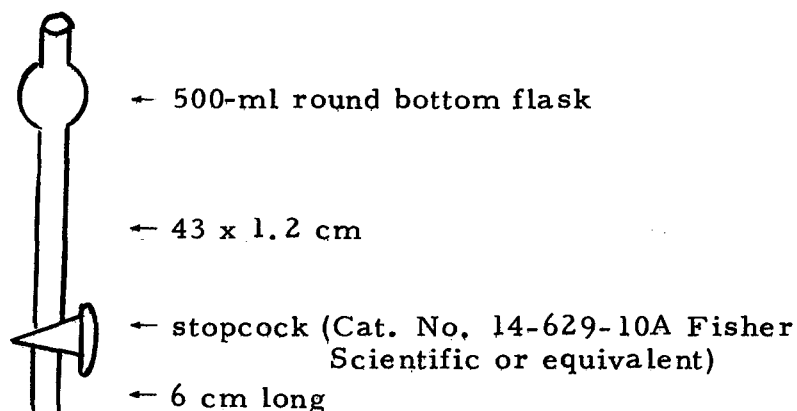


Figure 1. Liquid Chromatography Column

ELUTION SOLVENT MIXTURES

TABLE I

<u>Heptane</u>	<u>Benzene</u>
IA 45 ml	5 ml
IB 40 ml	10 ml
IC 35 ml	15 ml
ID 30 ml	20 ml
IE 25 ml	25 ml
IF 20 ml	30 ml
IG 15 ml	35 ml
IH 10 ml	40 ml
II 5 ml	45 ml
	50 ml

TABLE II

<u>Benzene</u>	<u>Chloroform</u>
IIA 45 ml	5 ml
IIB 35 ml	15 ml
IIC 25 ml	25 ml
IID 15 ml	35 ml
IIE 5 ml	45 ml
	50 ml

TABLE III

<u>Chloroform</u>	<u>Ethanol</u>
IIIA 45 ml	5 ml
IIIB 25 ml	25 ml
IIIC 15 ml	35 ml
	50 ml

TABLE IV

<u>Ethanol</u>	<u>Water</u>
IIID 40 ml	10 ml
IIIE 30 ml	20 ml

APPENDIX B

CONTENTS

<u>TABLE</u>	<u>TITLE</u>
I	Fixed Samplers, Round I, Benzene Soluble
II	Fixed Samplers, Round II, Benzene Soluble
III	Fixed Samplers, Round I, BaP
IV	Fixed Samplers, Round II, BaP
V	Fixed Samplers, Round I, L.C. For 9 PNA's
VI	Fixed Samplers, Round II, L.C. For 9 PNA's
VII	Fixed Samplers, Round I, GC-UV For 14 PNA's
VIII	Fixed Samplers, Round II, GC-UV For 14 PNA's
IX	High-Volume, Round I, B.S., BaP, L.C.
X	High-Volume, Round II, B.S., BaP, L.C.
XI	High-Volume, Round I, AA For 6 Metals
XII	High-Volume, Round II, AA For 6 Metals
XIII	High-Volume, Round I, GC-UV For 14 PNA's
XIV	High-Volume, Round II, GC-UV For 14 PNA's
XV	Personals, Round I, B.S., BaP
XVI	Personals, Round II, B.S., BaP
XVII	Personals, Round I, GC-UV For 14 PNA's
XVIII	Personals, Round II, GC-UV For 14 PNA's
XIX	Charcoal Tubes, Round I, GC For 4 Solvents
XX	Charcoal Tubes, Round II, GC For 4 Solvents

The abbreviations used throughout the tables are:

N.D.	None detected This notation means that the amount of the compound on the filter was below the detection limit of the method. All detection limits are given in Section III: Results, in the discussion of the individual methods.
D.O.	Dorr-Oliver cyclone
G.G.	Gross - glass; a glass fiber filter held in a Millipore Field Monitor Cassette to collect a gross sample.
G.S.	Gross - silver; a silver membrane filter held in a Millipore Field Monitor Cassette to collect a gross sample.
BCIRA	British Cast Iron Research Association cyclone
H.E.	Horizontal elutriator
B.S.	Benzene soluble fraction
Pyr	Pyrene
Flu	Fluoranthene
BaA	Benz(a)anthracene
Chr	Chrysene
BeP	Benzo(e)pyrene
Pery	Perylene
BkF	Benzo(k)fluoranthene
Ant	Anthanthrene
BaP	Benzo(a)pyrene
BcA	Benz(c)acridine
BaAn	Benz(a)anthrone
BbF	Benzo(b)fluoranthene
BjF	Benzo(j)fluoranthene

DBahA	Dibenz(a,h)anthracene
BghiP	Benzo(g,h,i)perylene

The column in Tables II through IX labeled "Other Analysis Done on Sample" indicates that the same sample was also analyzed by another method. The numbers appearing in this column refer to the methods listed in the beginning of this report. As an example, in Table II filter number GS-7 is listed as also being done by method 2, which is the GC-UV method for 14 PNA's. Therefore, GS-7 should also be listed in Table VIII.

The charcoal tube data is given in Tables XIX and XX. The "A" and "B" sections of the charcoal tube refer to the two distinct sections of each charcoal tube. The tube is completely described in PSM-1015, Section 4.4.1.

TABLE I

Fixed Samplers, Round I
Method 1, Benzene Soluble

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>B.S. mg/m³</u>	<u>Other Analysis Done on Sample</u>
S-121	D.O.	A-1	0.2	--
GS-7	G.G.	A-1	3.0	2
S-125	BCIRA	A-1	0.8	--
S-126	H.E.	A-1	0.6	2
S-158	D.O.	A-2	0.2	--
S-157	G.S.	A-2	0.5	--
GF-20	G.G.	A-2	1.2	3
S-162	BCIRA	A-2	<0.2	--
S-154	H.E.	A-2	0.2	3
SG-2	D.O.	A-3	0.7	--
SG-14	G.S.	A-3	0.9	--
GF-21	G.G.	A-3	2.2	4
SG-6	BCIRA	A-3	0.8	--
SG-3	H.E.	A-3	0.6	4
SG-13	D.O.	A-7	1.6	--
SG-12	G.S.	A-7	2.5	--
GF-35	G.G.	A-7	2.3	4
SG-9	BCIRA	A-7	1.4	--
SG-7	H.E.	A-7	1.2	4
S-130	D.O.	A-8	0.9	--
S-127	G.S.	A-8	1.8	--
GF-8	G.G.	A-8	1.8	3
S-134	BCIRA	A-8	0.5	--
S-132	H.E.	A-8	0.9	3
S-144	D.O.	A-9	0.6	--
S-143	G.S.	A-9	0.7	--
GF-33	G.G.	A-9	1.3	2
S-142	BCIRA	A-9	0.6	--
S-149	H.E.	A-9	1.0	2

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>B.S. mg/m³</u>	<u>Other Analysis Done on Sample</u>
GSM-10	D.O.	B-1	2.1	--
GSGG-1	G.S.	B-1	7.2	--
GSGG-4	G.G.	B-1	6.5	2
GSM-12	BCIRA	B-1	14.4	--
GSGM-4	H.E.	B-1	2.9	2
GSM-3	D.O.	B-2	0.7	--
GSM-4	G.S.	B-2	1.1	--
GSG-33	G.G.	B-2	0.7	3
GSM-2	BCIRA	B-2	0.7	--
GSM-1	H.E.	B-2	0.6	3
GSG-31	D.O.	B-3	1.3	--
GSG-32	G.S.	B-3	1.7	--
GSM-5	G.G.	B-3	1.9	4
GSG-30	BCIRA	B-3	1.2	--
GSG-34	H.E.	B-3	0.4	4
GSM-24	D.O.	B-7	1.8	--
GM-5	G.S.	B-7	23.2	--
GG-4	G.G.	B-7	5.0	3
GSM-11	BCIRA	B-7	9.1	--
GSM-23	H.E.	B-7	5.6	3
GSG-20	D.O.	B-8	1.2	--
GSG-17	G.S.	B-8	0.6	--
GG-6	G.G.	B-8	3.4	2
GSG-16	BCIRA	B-8	1.5	--
GSG-19	H.E.	B-8	2.0	2
GSM-22	D.O.	B-9	2.4	--
GG-5	G.G.	B-9	4.6	4
GSM-27	BCIRA	B-9	1.9	--
GSM-29	H.E.	B-9	2.5	4
GSM-30	BCIRA	B-5	0.8	5
GSC-45	D.O.	C-1	4.7	--
GSC-44	G.S.	C-1	4.3	2
GSM-34	G.G.	C-1	5.1	--
GSG-43	BCIRA	C-1	1.0	--
GSG-48	H.E.	C-1	1.1	2

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>B.S. mg/m³</u>	<u>Other Analysis Done on Sample</u>
GSM-32	G.S.	C-2	1.6	2
GSG-42	G.G.	C-2	1.1	--
GSM-36	BCIRA	C-2	0.1	--
GSM-37	H.E.	C-2	0.4	2
GSG-41	D.O.	C-3	1.0	--
GSG-38	G.S.	C-3	0.9	3
GSM-31	G.G.	C-3	0.8	--
GSG-40	BCIRA	C-3	0.5	--
GSG-39	H.E.	C-3	0.2	3
GSG-63	D.O.	C-7	1.5	--
GSG-57	G.S.	C-7	8.2	3
GG-8	G.G.	C-7	4.4	--
GSG-56	BCIRA	C-7	2.3	--
GSG-58	H.E.	C-7	2.5	3
GSM-40	D.O.	C-8	0.7	--
GSM-49	G.S.	C-8	2.8	4
GM-14	G.G.	C-8	3.4	--
GSM-46	BCIRA	C-8	1.3	--
GSM-39	H.E.	C-8	1.0	4
GSG-61	D.O.	C-9	0.4	--
GSG-59	G.S.	C-9	1.6	4
GG-7	G.G.	C-9	2.0	--
GSG-53	BCIRA	C-9	0.5	--
GSG-60	H.E.	C-9	0.6	4
GS-89	D.O.	D-1	1.4	--
GS-79	G.S.	D-1	2.7	2
GF-61	G.G.	D-1	3.2	--
GS-87	BCIRA	D-1	1.3	--
GS-74	H.E.	D-1	2.1	2
GS-86	D.O.	D-2	2.2	--
GS-85	G.S.	D-2	3.4	3
GF-65	G.G.	D-2	3.4	--
GS-88	BCIRA	D-2	2.1	--
GS-81	H.E.	D-2	2.4	3

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>B.S. mg/m³</u>	<u>Other Analysis Done on Sample</u>
GS-72	D.O.	D-3	0.4	--
GS-65	G.S.	D-3	0.9	2
GF-66	G.G.	D-3	0.6	--
GS-67	BCIRA	D-3	0.3	--
GS-71	H.E.	D-3	0.1	2
GS-91	D.O.	D-7	10.3	--
GS-58	G.S.	D-7	10.0	3
GF-52	G.G.	D-7	10.0	--
GS-57	BCIRA	D-7	8.9	--
GS-55	H.E.	D-7	9.9	3
GS-63	D.O.	D-8	4.7	--
GS-53	G.S.	D-8	5.4	4
GF-58	G.G.	D-8	5.3	--
GS-62	BCIRA	D-8	4.0	--
GS-61	H.E.	D-8	3.6	4
GS-50	D.O.	D-9	7.0	--
GS-56	G.S.	D-9	10.4	4
GF-50	G.G.	D-9	8.3	--
GS-52	BCIRA	D-9	5.8	--
GS-51	H.E.	D-9	5.2	4
GS-119	D.O.	E-1	0.2	2
GS-124	G.S.	E-1	2.6	--
GF-23	G.G.	E-1	1.3	--
GS-118	BCIRA	E-1	0.4	--
GS-109	H.E.	E-1	1.0	2
GS-105	D.O.	E-2	1.0	--
GS-107	G.S.	E-2	0.4	3
GF-25	G.G.	E-2	1.2	--
GS-108	BCIRA	E-2	0.1	--
GS-106	H.E.	E-2	1.0	3
GS-110	D.O.	E-3	1.0	--
GS-112	G.S.	E-3	2.7	2
GF-31	G.G.	E-3	2.0	--
GS-113	BCIRA	E-3	0.3	--
GS-114	H.E.	E-3	1.6	2

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>B.S. mg/m³</u>	<u>Other Analysis Done on Sample</u>
GS-141	D.O.	E-7	3.6	--
GS-96	G.S.	E-7	2.8	3
GS-97	BCIRA	E-7	1.0	--
GS-95	H.E.	E-7	2.5	3
GS-100	D.O.	E-8	1.6	--
GS-104	G.S.	E-8	2.0	4
GF-77	G.G.	E-8	2.0	--
GS-102	BCIRA	E-8	1.2	--
GS-101	H.E.	E-8	1.5	4
GS-41	D.O.	E-9	1.2	--
GS-133	G.S.	E-9	1.5	4
GS-132	BCIRA	E-9	0.7	--
GS-131	H.E.	E-9	1.3	4
GSG-65	BLANK		<0.1	
S-204	BLANK		<0.1	

TABLE II

Fixed Samplers, Round II
Method 1, Benzene Soluble

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>B.S. mg/m³</u>	<u>Other Analysis Done on Sample</u>
F-340	D.O.	A-21	4.0	--
F-344	G.S.	A-21	5.4	--
F-352	G.G.	A-21	5.5	2
F-345	BCIRA	A-21	3.0	--
F-349	H.E.	A-21	3.9	2
F-342	D.O.	A-22	1.5	--
F-357	G.S.	A-22	1.9	--
F-343	G.G.	A-22	2.4	3
F-338	BCIRA	A-22	1.1	--
F-339	H.E.	A-22	1.2	3
F-353	D.O.	A-26	1.1	--
F-303	G.S.	A-26	1.1	--
F-308	G.G.	A-26	0.1	4
F-305 ↑	BCIRA	A-26	1.5	--
F-372 ↓	BCIRA	A-26	0.4	--
F-356	H.E.	A-26	0.7	4
F-300	D.O.	A-28	1.3	--
F-309	G.S.	A-28	1.1	--
F-304 ↑	G.G.	A-28	1.4	3
F-371 ↓	G.G.	A-28	0.3	3
F-313	BCIRA	A-28	0.7	--
F-310	H.E.	A-28	0.7	3
F-302	D.O.	A-29	1.0	--
F-315	G.S.	A-29	0.8	--
F-318	G.G.	A-29	2.4	2
F-306	BCIRA	A-29	0.3	--
F-307	H.E.	A-29	1.1	2
F-334	D.O.	A-30	1.4	--
G-67	G.S.	A-30	22.0	--
F-301 ↑	G.G.	A-30	1.5	4
F-370 ↓	G.G.	A-30	0.5	4
F-333	BCIRA	A-30	6.8	--
F-325	H.E.	A-30	1.4	4

Preceding page blank

Filter No.	Sampler Type	Co. #	B.S. mg/m^3	Other Analysis Done on Sample
F-401 ↑	D.O.	B-24	2.6	--
F-473	D.O.	B-24	<0.1	--
F-474 ↓	D.O.	B-24	0.1	--
F-423	G.S.	B-24	3.7	--
F-418 ↑	G.G.	B-24	3.9	2
F-497 ↓	G.G.	B-24	0.1	2
F-402 ↑	BCIRA	B-24	2.6	--
F-475	BCIRA	B-24	<0.1	--
F-476 ↓	BCIRA	B-24	0.3	--
F-460	D.O.	B-25	1.0	--
F-413 ↑	G.S.	B-25	0.7	--
F-493 ↓	G.S.	B-25	<0.1	--
F-414 ↑	G.G.	B-25	0.6	4
F-494 ↓	G.G.	B-25	<0.1	4
F-457	BCIRA	B-25	1.0	--
F-403 ↑	H.E.	B-25	0.1	4
F-477	H.E.	B-25	<0.1	4
F-478 ↓	H.E.	B-25	<0.1	4
F-421	D.O.	B-27	4.7	--
F-466	G.S.	B-27	7.6	--
F-400 ↑	G.G.	B-27	7.7	3
F-471	G.G.	B-27	<0.1	3
F-472 ↓	G.G.	B-27	<0.1	3
F-405 ↑	BCIRA	B-27	3.5	--
F-479	BCIRA	B-27	<0.1	--
F-480 ↓	BCIRA	B-27	<0.1	--
F-420 ↑	H.E.	B-27	5.4	3
F-499 ↓	H.E.	B-27	<0.1	3
F-406 ↑	D.O.	B-28	1.8	--
F-481	D.O.	B-28	<0.1	--
F-482 ↓	D.O.	B-28	0.2	--
F-422	G.S.	B-28	2.8	--
F-410 ↑	G.G.	B-28	4.3	3
F-489	G.G.	B-28	0.1	3
F-490 ↓	G.G.	B-28	0.4	3
F-415 ↑	H.E.	B-28	2.3	3
F-495 ↓	H.E.	B-28	0.0	3

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>B.S. mg/m³</u>	<u>Other Analysis Done on Sample</u>
F-411 ↑	D.O.	B-29	4.0	--
F-492 ↓	D.O.	B-29	1.3	--
F-424	G.S.	B-29	4.9	--
G-82	G.G.	B-29	7.1	2
F-409 ↑	BCIRA	B-29	4.3	--
F-487	BCIRA	B-29	1.2	--
F-488 ↓	BCIRA	B-29	0.2	--
F-416 ↑	H.E.	B-29	3.9	2
F-496 ↓	H.E.	B-29	0.0	2
F-419 ↑	D.O.	B-30	1.6	--
F-498 ↓	D.O.	B-30	<0.1	--
F-440	G.S.	B-30	3.0	--
F-407 ↑	BCIRA	B-30	1.9	--
F-483	BCIRA	B-30	<0.1	--
F-484 ↓	BCIRA	B-30	<0.1	--
F-435	H.E.	B-30	2.2	4
F-408 ↑	D.O.	B-31	2.4	--
F-485	D.O.	B-31	<0.2	--
F-486 ↓	D.O.	B-31	0.3	--
F-445	G.S.	B-31	2.6	--
G-85	G.G.	B-31	3.7	4
F-431	BCIRA	B-31	1.3	--
F-442	H.E.	B-31	1.2	4
F-63	D.O.	C-21	1.2	--
F-57	G.S.	C-21	4.5	2
G-2	G.G.	C-21	2.4	--
F-55	BCIRA	C-21	0.8	--
F-58	H.E.	C-21	2.2	2
F-59	D.O.	C-22	<0.1	--
F-56	G.S.	C-22	1.1	2
G-3	G.G.	C-22	0.8	--
F-60	BCIRA	C-22	0.1	--
F-52	H.E.	C-22	0.5	2
F-62	D.O.	C-23	0.6	--
F-54	G.S.	C-23	0.8	3
G-1	G.G.	C-23	0.6	--
F-53	BCIRA	C-23	0.7	--
F-51	H.E.	C-23	0.6	3

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>B.S. mg/m³</u>	<u>Other Analysis Done on Sample</u>
F-1	D.O.	C-27	1.1	--
F-66	G.S.	C-27	2.4	3
G-18	G.G.	C-27	2.4	--
F-15	BCIRA	C-27	1.0	--
F-4	H.E.	C-27	0.8	3
F-9	D.O.	C-28	1.6	--
F-5	G.S.	C-28	2.5	4
G-20	G.G.	C-28	2.5	--
F-8	BCIRA	C-28	1.0	--
F-7	H.E.	C-28	0.9	4
F-13	D.O.	C-29	5.0	--
F-12	G.S.	C-29	2.9	4
F-18	G.G.	C-29	4.8	--
F-14	BCIRA	C-29	2.8	--
F-10	H.E.	C-29	4.1	4
G-29	G.G.	D-21	2.9	--
F-132	G.S.	D-21	4.2	2
F-120	D.O.	D-26	4.4	--
F-112	G.S.	D-26	5.9	3
G-27	G.G.	D-26	5.2	--
F-118	BCIRA	D-26	12.8	--
F-130	H.E.	D-26	4.1	3
F-114	D.O.	D-27	8.1	--
F-143	G.S.	D-27	12.4	4
G-23	G.G.	D-27	10.5	--
F-153	BCIRA	D-27	6.1	--
F-152	H.E.	D-27	6.7	4
F-104	D.O.	D-28	9.8	--
F-103 †	G.S.	D-28	3.3	3
F-182	G.S.	D-28	3.4	3
F-183 †	G.S.	D-28	0.8	3
F-100	G.G.	D-28	10.3	--
F-148	BCIRA	D-28	5.5	--
F-101	H.E.	D-28	7.5	3

Filter No.	Sampler Type	Co. #	B.S. mg/m ³	Other Analysis Done on Sample
F-146	D.O.	D-29	8.6	--
F-147	G.S.	D-29	10.6	4
G-25	G.G.	D-29	10.1	--
F-141	BCIRA	D-29	11.7	--
F-142	H.E.	D-29	8.6	4
F-105 †	D.O.	D-30	11.1	2
F-180	D.O.	D-30	1.2	2
F-181 †	D.O.	D-30	0.7	2
F-211	G.S.	E-21	4.4	2
G-49	G.G.	E-21	3.4	--
F-250	BCIRA	E-21	1.0	--
F-216	H.E.	E-21	4.5	2
F-259	D.O.	E-22	2.1	--
F-255	G.S.	E-22	2.8	3
G-45	G.G.	E-22	3.9	--
F-217	H.E.	E-22	3.8	3
F-256	D.O.	E-23	1.6	--
F-212	G.S.	E-23	4.9	2
G-55	G.G.	E-23	1.5	--
F-210	H.E.	E-23	4.1	2
F-208 †	D.O.	E-24	2.8	5
F-270 †	D.O.	E-24	0.5	5
F-204 †	G.S.	E-24	3.0	3+5
F-267	G.S.	E-24	0.1	3+5
F-268 †	G.S.	E-24	0.1	3+5
F-209 †	H.E.	E-24	2.1	3+5
F-271 †	H.E.	E-24	1.8	3+5
F-202 †	BCIRA	E-26	2.6	5
F-263	BCIRA	E-26	0.1	5
F-264 †	BCIRA	E-26	0.6	5
F-232	D.O.	E-27	6.4	--
F-200	G.S.	E-27	2.8	4
F-261	G.S.	E-27	0.9	4
F-262	G.S.	E-27	0.1	4
G-50	G.G.	E-27	4.0	--
F-251	H.E.	E-27	2.0	4

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>B.S. mg/m³</u>	<u>Other Analysis Done on Sample</u>
G-42	G.S.	E-28	3.8	3
G-43	G.G.	E-28	2.1	--
F-215	H.E.	E-28	2.3	3
F-207 ↑	D.O.	E-29	1.5	--
F-269 ↓	D.O.	E-29	1.3	--
F-206	G.S.	E-29	1.8	4
F-222	G.G.	E-29	0.1	--
F-205	BCIRA	E-29	2.1	--
F-220	H.E.	E-29	1.2	4
F-203 ↑	H.E.	E-25	1.2	4+5
F-265	H.E.	E-25	0.1	4+5
F-266 ↓	H.E.	E-25	<0.1	4+5
G-62	BLANK		0.2	
G-6	BLANK		<0.1	
F-38	BLANK		<0.1	

TABLE III

Fixed Samplers, Round I
Method 3, BaP

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>BaP $\mu\text{g}/\text{m}^3$</u>	<u>Other Analysis Done on Sample</u>
GF-20	G.G.	A-2	18.68	1
S-154	H.E.	A-2	7.70	1
GF-28	G.G.	A-5	14.05	5
S-164,150,166	H.E.	A-5	8.46	5
GF-8	G.G.	A-8	20.56	1
S-132	H.E.	A-8	17.93	1
GSG-1	G.G.	A-12	2.44	5
GSG-33	G.G.	B-2	13.62	1
GSM-1	H.E.	B-2	14.62	1
GSM-21,19	G.G.	B-6	75.62	5
GSG-26,36	H.E.	B-6	51.57	5
GG-4	G.G.	B-7	21.60	1
GSM-23	H.E.	B-7	29.95	1
GSG-18	G.G.	B-10	2.56	5
GSG-8	H.E.	B-10	26.50	5
GSG-38	G.S.	C-3	4.43	1
GSG-39	H.E.	C-3	0.34	1
GSM-33	G.S.	C-6	12.69	5
GSM-45	H.E.	C-6	12.75	5
GSG-57	G.S.	C-7	27.17	1
GSG-58	H.E.	C-7	10.83	1
GSM-47	H.E.	C-10	3.09	5
GS-85	G.S.	D-2	25.01	1
GS-81	H.E.	D-2	14.41	1
GS-66	G.S.	D-4	11.11	5
GS-73	H.E.	D-4	11.65	5
GS-58	G.S.	D-7	87.94	1
GS-55	H.E.	D-7	59.73	1
GS-54	G.S.	D-11	60.73	5
GS-49	H.E.	D-11	48.08	5
GS-107	G.S.	E-2	10.30	1
GS-106	H.E.	E-2	0.90	1
GS-129	G.S.	E-4	11.34	5
GS-123	H.E.	E-4	9.11	5
GS-96	G.S.	E-7	27.51	1
GS-95	H.E.	E-7	22.92	1
GS-115	G.S.	E-11	14.53	5
GS-136	H.E.	E-11	16.51	5
GSG-65	BLANK		2.00	

TABLE IV

Fixed Samplers, Round II
Method 3, BaP

<u>Filter No.</u>	<u>Sampler Type</u>	<u>Co. #</u>	<u>BaP $\mu\text{g}/\text{m}^3$</u>	<u>Other Analysis Done on Sample</u>
F-343	G.G.	A-22	6.22	1
F-339	H.E.	A-22	7.56	1
F-359	G.G.	A-25	23.73	5
F-351	H.E.	A-25	11.84	5
F-304	G.G.	A-28	6.46	1
F-310	H.E.	A-28	5.46	1
F-335	G.G.	A-32	3.10	5
F-314	H.E.	A-32	4.83	5
G-83	G.G.	B-22	49.31	5
F-463	H.E.	B-22	24.41	5
F-400	G.G.	B-27	20.18	1
F-420	H.E.	B-27	22.12	1
F-410	G.G.	B-28	16.03	1
F-415	H.E.	B-28	17.98	1
F-432	G.G.	B-32	28.05	5
F-441	H.E.	B-32	46.86	5
F-54	G.S.	C-23	10.40	1
F-51	H.E.	C-23	10.65	1
F-74	G.S.	C-26	7.14	5
F-68	H.E.	C-26	16.13	5
F-66	G.S.	C-27	11.32	1
F-4	H.E.	C-27	9.13	1
F-3	G.S.	C-30	26.36	5
F-23	H.E.	C-30	10.38	5
F-112	G.S.	D-26	50.96	1
F-130	H.E.	D-26	29.19	1
F-103†	G.S.	D-28	17.82	1
F-182	G.S.	D-28	20.11	1
F-183†	G.S.	D-28	9.20	1
F-101	H.E.	D-28	58.86	1
G-34	G.S.	D-31	23.37	5
F-140	H.E.	D-31	17.88	5
F-255	G.S.	E-22	9.56	1
F-217	H.E.	E-22	12.78	1
F-221	BCIRA	E-27	7.22	1+5
G-42	G.S.	E-28	9.95	1
F-253	BCIRA	E-28	4.88	1+5
F-215	H.E.	E-28	15.90	1
G-57	G.S.	E-31	2.59	5
F-246	H.E.	E-31	1.33	5

TABLE V

FIELD SAMPLERS, ROUND 1
METHOD 4, LIQUID CHROMATOGRAPHY

 $\mu\text{g}/\text{m}^3$

Filter No.	Sampler type	Co.#	Other analysis done on sample	Pyr	Flu	BaA	Chr	BeP	Pery	BkF	Ant	BaP
GF-21	G.G.	A-3	1	3.9	5.6	16.5	9.7	5.7	N.D.	9.1	N.D.	15.4
SG-3	H.E.	A-3	1	0.8	<0.6	8.7	4.8	3.5	N.D.	6.1	N.D.	9.3
GF-6	G.G.	A-6	5	<0.5	N.D.	6.7	4.0	3.4	1.3	3.8	N.D.	8.3
SG-5	H.E.	A-6	5	0.6	N.D.	5.6	3.2	3.5	1.2	3.6	0.7	18.0
GF-35	G.G.	A-7	1	4.7	5.3	12.2	7.1	4.4	1.0	7.1	N.D.	14.2
SG-7	H.E.	A-7	1	6.3	11.5	10.9	5.1	3.8	<0.6	4.2	N.D.	15.5
SG-133	G.G.	A-10	5	4.0	3.4	12.0	6.3	4.8	2.2	5.1	1.8	20.0
SG-16	H.E.	A-10	5	2.2	1.8	8.0	3.8	3.2	1.5	3.8	1.1	15.6
GSM-5	G.G.	B-3	1	2.3	24.1	16.9	7.8	3.2	2.0	7.8	1.3	21.7
GSG-34	H.E.	B-3	1	6.8	10.8	14.2	7.4	3.5	2.7	6.8	0.6	19.4
GSGG-2	G.G.	B-5	5	43.4	56.4	73.3	44.0	39.4	44.5	30.4	3.8	95.8
GSGM-3,1	H.E.	B-5	5	34.4	47.6	63.1	48.2	43.6	43.6	43.0	23.0	126.3
GG-5	G.G.	B-9	1	2.3	29.2	27.2	9.9	8.4	<0.5	10.9	N.D.	37.7
GSM-29	H.E.	B-9	1	30.3	44.5	15.7	8.6	6.1	3.7	7.6	2.8	31.3
GM-1	G.G.	B-11	5	8.9	8.9	14.4	6.1	5.5	3.2	5.0	2.6	21.6
GSM-7	H.E.	B-11	5	5.8	4.9	10.4	6.9	6.9	4.7	5.1	3.4	26.5
GSM-49	G.S.	C-8	1	4.0	5.5	22.6	10.1	5.9	3.7	8.6	0.9	32.8
GSM-39	H.E.	C-8	1	<0.9	N.D.	16.4	11.8	7.5	3.9	6.4	<0.9	20.0
GSG-59	G.S.	C-9	1	N.D.	N.D.	8.8	4.9	3.8	1.5	4.5	N.D.	11.5
GSG-60	H.E.	C-9	1	2.1	2.6	9.1	5.8	4.5	2.0	3.9	1.0	17.5
GG-14	G.S.	C-11	5	3.6	N.D.	11.7	5.3	6.7	5.2	8.4	1.7	45.3
GG-15	H.E.	C-11	5	7.6	5.1	25.1	12.6	6.6	5.0	10.0	2.2	41.5
GSG-67	G.S.	C-12	5	4.4	4.9	13.8	6.9	6.9	3.9	9.4	1.5	38.4
GSG-71	H.E.	C-12	5	4.2	6.2	19.4	9.0	5.7	3.8	9.9	0.8	36.0
GS-53	G.S.	D-8	1	44.5	129.7	77.8	44.5	18.5	10.7	35.6	4.8	55.6
GS-61	H.E.	D-8	1	23.1	33.0	98.7	45.5	20.5	10.2	29.6	4.9	53.1
GS-56	G.S.	D-9	1	37.0	53.8	47.1	19.8	10.1	4.7	5.7	1.2	67.3
GS-51	H.E.	D-9	1	23.0	36.1	29.5	N.D.	5.2	4.3	6.6	2.4	45.0
GS-42	G.S.	D-10	5	41.3	50.0	40.8	16.8	15.8	6.1	20.4	N.D.	81.5
GS-45	H.E.	D-10	5	30.6	25.7	36.5	17.8	11.4	4.7	13.8	1.8	138.2
	G.S.	D-12	5	159.1	302.9	174.5	82.1	51.3	25.2	71.9	13.3	225.9
	G.S.	E-8	1	12.1	12.6	9.0	7.5	1.7	1.0	3.0	0.8	20.6
	H.E.	E-8	1	12.0	17.2	11.5	8.4	2.1	2.1	2.5	0.8	24.0

1 SAMPLERS, ROUND I

sample lost; value corrected to adjust approximately for whole sample

TABLE VI

-----) SAMPLERS, ROUND II
METHOD 4, LIQUID CHROMATOGRAPHY

µg/m³

Filter No.	Sampler type	Co.#	Other analysis done on sample	Pyr	Flu	BaA	Chr	BeP	Pery	BkF	Ant	BeP
F-341	G.G.	A-23	5	N.D.	N.D.	<1.2	<1.2	<1.2	N.D.	N.D.	N.D.	3.4
F-347	H.E.	A-23	5	<0.5	N.D.	1.0	<0.5	N.D.	N.D.	N.D.	N.D.	0.8
F-308	G.G.	A-26	1	3.9	4.4	11.2	6.2	3.6	2.3	4.3	<1.4	16.6
F-356	H.E.	A-26	1	4.1	4.3	10.7	6.2	3.0	1.5	3.6	0.8	19.2
F-323	G.G.	A-27	5	N.D.	N.D.	8.6	7.2	<1.4	N.D.	3.0	N.D.	8.9
F-319	H.E.	A-27	5	3.0	6.7	7.9	0.6	3.4	2.8	2.0	1.2	13.5
F-301	G.G.	A-30	1	4.5	12.6	8.9	4.6	3.1	<1.3	4.3	<1.3	19.1
F-325	H.E.	A-30	1	8.6	15.6	9.6	5.0	3.0	1.3	2.6	0.9	15.6
F-450	G.G.	B-23	5	4.4	4.8	13.1	9.1	3.9	3.6	6.8	2.3	14.2
F-468	H.E.	B-23	5	7.9	7.9	13.8	10.3	6.4	3.0	6.9	0.7	13.8
F-414	G.G.	B-25	1	<1	N.D.	<1.1	<1.1	<1.1	<1.1	N.D.	N.D.	3.1
F-403	H.E.	B-25	1	<0.5	N.D.	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.7
G-85	G.G.	B-31	1	5.7	12.0	18.4	10.5	4.0	3.1	<1.4	1.8	22.7
F-442	H.E.	B-31	1	3.3	1.9	14.0	10.1	4.8	2.2	8.4	0.8	1.5
F-5	G.S.	C-28	1	18.3	20.1	20.1	10.3	8.5	4.9	2.6	5.8	25.4
F-7	H.E.	C-28	1	9.7	7.4	21.3	5.1	6.0	3.7	4.4	4.0	25.9
F-12	G.S.	C-29	1	45.8	106.1	39.7	19.0	10.0	6.7	11.7	3.9	67.0
F-10	H.E.	C-29	1	222.2	296.3	50.9	27.3	35.6	21.3	1.6	33.8	90.3
F-27	G.S.	C-31	5	13.5	16.5	40.6	9.0	9.0	8.3	12.0	4.1	52.6
F-33	H.E.	C-31	5	26.4	47.1	32.1	14.3	7.8	6.0	12.1	3.1	39.3
F-24	G.S.	C-32	5	23.3	45.9	31.4	17.6	8.2	5.2	11.9	2.6	35.8
F-6	H.E.	C-32	5	18.8	29.2	28.6	13.6	7.8	5.1	10.4	2.3	45.4
F-143	G.S.	D-27	1	70.6	117.6	35.9	21.8	7.6	5.9	7.6	7.6	76.5
F-152	H.E.	D-27	1	54.5	103.0	35.1	20.6	11.5	9.1	2.6	9.7	78.8
F-147	G.S.	D-29	1	186.9	424.2	131.3	75.8	27.3	26.8	48.5	12.1	217.2
F-142	H.E.	D-29	1	147.2	350.2	147.2	76.1	25.4	13.2	33.0	4.8	167.5
F-106	G.S.	D-30	5	109.8	242.8	63.6	32.9	13.9	8.7	18.5	0.6	32.9
F-102	H.E.	D-30	5	146.2	345.0	70.2	33.9	16.4	9.9	25.7	0.8	54.4
F-109	G.S.	D-32	5	60.0	145.0	44.0	17.5	11.0	8.0	13.5	3.0	65.0
F-137	H.E.	D-32	5	60.6	131.3	41.4	20.7	10.1	6.6	11.1	3.4	65.6
	G.S.	E-25	5	5.1	3.9	11.0	7.4	3.0	2.2	3.9	1.2	22.6
	G.S.	E-27	1	26.1	32.4	12.2	7.4	4.5	3.0	<0.5	3.3	37.2
	H.E.	E-27	1	19.9	27.0	10.7	7.1	3.9	2.5	1.3	3.2	40.8
	D.O.	E-28	5	20.4	29.2	23.3	16.0	8.2	5.5	9.8	1.7	49.6

B-23

FIELD SAMPLERS, ROUND II METHOD 4, LIQUID CHROMATOGRAPHY

 $\mu\text{g}/\text{m}^3$ [illegible]

6-24

TABLE VII

FIXED SAMPLERS, ROUND I
METHOD 2, GC-UV for 14 PNA's

µg/m³

Filter No.	Sampler type	Co.#	Other analysis done on sample	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BeP	DBahA	BghiP	Ant
GS-7	G.G.	A-1	1	N.D.	1.74	N.D.	8.09	9.34	N.D.	7.47	2.30	5.10	8.71	12.45	N.D.	5.91	0.87
S-126	H.E.	A-1	1	N.D.	N.D.	2.67	5.51	5.51	N.D.	3.45	1.65	3.49	5.06	10.11	N.D.	5.06	1.65
GF-4	G.G.	A-4	5	5.06	4.40	N.D.	6.54	9.52	N.D.	4.76	3.81	5.29	4.46	7.73	N.D.	4.82	1.25
S-203	H.E.	A-4	5	2.73	1.20	2.19	5.47	4.70	N.D.	3.88	3.50	N.D.	5.25	7.65	N.D.	5.25	1.31
GF-33	G.G.	A-9	1	0.69	0.60	N.D.	5.55	6.47	N.D.	3.05	2.13	2.64	6.47	5.55	N.D.	2.77	0.78
S-149	H.E.	A-9	1	0.59	N.D.	N.D.	7.53	9.69	N.D.	4.57	1.45	4.09	4.47	10.23	N.D.	N.D.	0.54
S-205	G.G.	A-11	5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-7	H.E.	A-11	5	N.D.	N.D.	N.D.	1.08	1.68	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-4	G.G.	B-1	1	6.82	N.D.	N.D.	18.70	27.50	N.D.	15.40	4.51	9.24	12.10	26.40	N.D.	N.D.	N.D.
GSGM-4	H.E.	B-1	1	8.49	4.19	N.D.	16.99	21.52	N.D.	13.59	3.28	9.51	10.87	23.78	N.D.	8.49	6.80
GSG-28	G.G.	B-4	5	N.D.	1.18	N.D.	0.69	1.08	N.D.	N.D.	N.D.	N.D.	N.D.	4.24	N.D.	N.D.	N.D.
GSM-15	H.E.	B-4	5	46.35	53.24	N.D.	22.68	28.60	N.D.	N.D.	9.17	14.79	12.82	46.35	28.60	N.D.	N.D.
GG-6	G.G.	B-8	1	14.93	14.93	N.D.	14.93	23.12	N.D.	8.19	2.02	6.74	6.74	17.82	N.D.	8.67	4.24
GSG-19	H.E.	B-8	1	2.34	12.46	N.D.	21.93	34.90	N.D.	17.95	3.64	11.96	9.47	26.92	N.D.	18.94	7.98
GG-3	G.G.	B-12	5	15.11	14.55	N.D.	10.08	14.55	N.D.	3.86	2.24	4.42	4.70	10.63	N.D.	6.72	2.80
GSM-8	H.E.	B-12	5	12.53	13.67	N.D.	10.25	15.38	N.D.	8.54	1.82	5.70	N.D.	15.38	N.D.	7.98	3.93
GSG-44	G.S.	C-1	1	1.65	2.87	14.34	6.62	9.38	N.D.	0.50	1.49	3.09	3.75	7.17	N.D.	3.92	0.83
GSG-48	H.E.	C-1	1	1.30	1.79	N.D.	10.28	12.99	N.D.	9.74	2.54	5.95	8.12	N.D.	N.D.	5.95	4.38
GSM-32	G.S.	C-2	1	2.77	1.81	N.D.	10.19	13.59	N.D.	8.49	1.81	5.55	6.80	14.72	2.38	6.79	1.76
GSM-37	H.E.	C-2	1	N.D.	N.D.	6.73	5.22	4.66	N.D.	5.22	2.92	3.48	3.25	10.66	N.D.	N.D.	N.D.
GSG-49	G.S.	C-4	5	1.04	1.22	N.D.	0.50	0.81	N.D.	N.D.	N.D.	N.D.	0.72	1.67	N.D.	4.00	0.86
GSG-51	H.E.	C-4	5	N.D.	N.D.	N.D.	3.17	3.30	N.D.	1.01	1.28	1.79	2.52	4.08	N.D.	2.57	0.46
GSG-55	G.S.	C-5	5	3.39	3.44	2.38	9.12	9.62	N.D.	2.13	1.57	5.06	5.06	9.12	2.38	5.06	1.17
GSG-54	H.E.	C-5	5	1.24	1.39	4.67	N.D.	1.74	N.D.	0.70	1.39	3.78	2.09	6.97	1.54	5.47	0.99
GS-79	G.S.	D-1	1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GS-74	H.E.	D-1	1	3.43	2.63	n.D.	7.52	9.40	N.D.	4.37	4.37	3.43	3.43	10.34	1.17	4.28	1.41
GS-65	G.S.	D-3	1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GS-71	H.E.	D-3	1	N.D.	N.D.	N.D.	0.57	0.95	N.D.	1.34	N.D.	0.62	0.81	2.38	N.D.	N.D.	N.D.
GS-82	G.S.	D-5	5	56.28	42.21	5.63	36.58	60.98	N.D.	28.61	5.63	16.89	18.29	45.50	27.20	20.17	10.79
	H.E.	D-5	5	16.57	41.65	7.16	49.26	80.61	N.D.	23.73	7.16	21.05	8.51	22.84	3.90	20.15	11.20
	G.S.	D-6	5	6.05	5.58	4.51	8.37	12.56	N.D.	3.63	1.35	2.98	3.72	6.98	N.D.	3.12	6.05
	H.E.	D-6	5	3.12	1.45	8.14	16.73	14.47	N.D.	N.D.	2.98	3.12	3.25	7.23	5.42	4.52	0.04

B-25

$\mu\text{g}/\text{m}^3$

FIXED SAMPLERS, ROUND 1

[illegible]

6-26

TABLE VIII

FIXED SAMPLERS, ROUND II
METHOD 2, GC-UV for 14 PNA's

$\mu\text{g}/\text{m}^3$

Filter No.	Sampler type	Co.#	Other analysis done on sample	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBaH	BghIP	Ant
F-352	G.G.	A-21	1	31.96	22.83	N.D.	16.74	19.79	N.D.	10.35	3.81	7.00	7.91	15.22	N.D.	14.76	2.74
F-349	H.E.	A-21	1	20.86	15.34	N.D.	6.13	10.43	N.D.	8.59	2.15	5.34	4.72	10.43	N.D.	9.20	2.09
F-355	G.G.	A-24	5	7.16	10.89	4.44	14.33	18.62	N.D.	10.46	3.87	7.16	11.17	18.62	N.D.	14.33	1.86
F-346	H.E.	A-24	5	2.25	20.81	N.D.	19.08	17.34	N.D.	28.32	3.93	9.25	8.09	20.81	4.86	13.29	2.66
F-318	G.G.	A-29	1	5.24	4.36	N.D.	7.36	7.61	N.D.	2.24	N.D.	2.00	1.37	5.86	N.D.	N.D.	N.D.
F-307	H.E.	A-29	1	N.D.	1.24	N.D.	5.97	6.47	N.D.	4.88	1.19	2.99	2.99	4.23	N.D.	N.D.	N.D.
F-321	G.G.	A-31	5	N.D.	N.D.	N.D.	4.81	6.33	N.D.	N.D.	N.D.	N.D.	3.71	N.D.	N.D.	N.D.	N.D.
F-311	H.E.	A-31	5	N.D.	1.29	N.D.	6.74	9.55	N.D.	7.86	N.D.	4.38	3.76	N.D.	N.D.	N.D.	N.D.
F-462	G.G.	B-21	5	16.51	22.02	N.D.	44.04	62.39	N.D.	33.03	8.62	23.85	23.85	55.05	N.D.	18.35	N.D.
F-456	H.E.	B-21	5	33.59	34.35	N.D.	31.30	52.67	N.D.	42.75	4.73	12.98	15.27	39.69	10.69	20.61	6.49
F-418	G.G.	B-24	1	4.21	11.70	N.D.	14.04	16.37	N.D.	10.64	3.16	10.29	8.65	N.D.	N.D.	15.20	4.33
G-81	G.G.	B-26	5	N.D.	N.D.	N.D.	1.59	1.25	N.D.	6.92	3.97	9.19	4.65	N.D.	N.D.	N.D.	N.D.
F-461	H.E.	B-26	5	N.D.	N.D.	N.D.	5.53	4.10	N.D.	10.14	5.07	13.82	N.D.	N.D.	N.D.	N.D.	N.D.
G-82	G.G.	B-29	1	37.74	46.61	6.88	34.41	56.60	N.D.	13.32	3.33	11.10	21.09	44.04	N.D.	24.42	5.99
F-416	H.E.	B-29	1	50.23	59.36	3.42	32.42	34.70	N.D.	18.26	5.02	13.24	15.53	35.16	5.48	95.89	6.39
F-57	G.S.	C-21	1	5.04	4.43	2.32	11.07	16.06	N.D.	11.07	2.05	5.54	7.75	16.06	3.99	13.29	2.27
F-58	H.E.	C-21	1	3.03	4.26	N.D.	10.11	13.83	N.D.	11.17	2.13	5.32	7.45	14.89	N.D.	7.45	2.39
F-56	G.S.	C-22	1	1.35	N.D.	N.D.	0.24	2.86	N.D.	1.16	1.11	1.36	0.97	2.18	N.D.	N.D.	N.D.
F-52	H.E.	C-22	1	N.D.	N.D.	N.D.	0.70	0.90	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
F-61	G.S.	C-24	5	N.D.	N.D.	N.D.	6.90	8.18	N.D.	N.D.	N.D.	N.D.	3.82	7.82	N.D.	N.D.	N.D.
F-73	H.E.	C-24	5	N.D.	N.D.	N.D.	4.21	7.37	N.D.	7.54	N.D.	3.86	4.04	10.53	N.D.	N.D.	N.D.
F-70	G.S.	C-25	5	20.99	6.68	N.D.	20.99	61.07	N.D.	24.81	16.22	15.27	49.62	47.71	N.D.	N.D.	N.D.
F-75	H.E.	C-25	5	4.92	5.37	N.D.	16.10	21.47	N.D.	14.31	3.49	8.94	9.84	19.68	N.D.	11.63	49.19
F-132	G.S.	D-21	1	14.94	13.79	N.D.	22.41	30.46	N.D.	12.07	4.54	9.20	6.32	19.54	N.D.	8.05	1.49
F-115	G.S.	D-24	5	33.92	35.09	2.05	16.37	28.07	N.D.	10.53	3.16	8.77	7.60	18.31	N.D.	9.36	2.69
F-119	H.E.	D-24	5	22.44	17.31	2.95	12.82	19.87	N.D.	6.03	2.56	5.13	5.77	13.46	N.D.	8.33	3.33
F-116	G.S.	D-25	5	40.98	29.27	3.80	19.02	30.73	N.D.	3.17	1.17	2.58	10.24	24.88	36.58	9.27	2.88
F-105	D.O.	D-30	1	43.05	38.08	N.D.	34.77	51.32	N.D.	19.87	6.95	18.21	N.D.	N.D.	N.D.	61.26	5.79
F-180	D.O.	D-30	1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
F-181	D.O.	D-30	1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
F-181	G.S.	E-21	1	N.D.	N.D.	N.D.	6.47	5.24	N.D.	3.35	N.D.	3.06	3.06	5.88	N.D.	N.D.	N.D.
F-181	H.E.	E-21	1	N.D.	N.D.	N.D.	5.75	3.91	N.D.	3.28	N.D.	2.99	2.99	4.25	N.D.	N.D.	N.D.
F-181	G.S.	E-23	1	1.25	2.64	N.D.	10.42	11.11	N.D.	8.33	2.01	6.32	5.07	6.94	N.D.	N.D.	N.D.

B-27

FIXED SAMPLERS, ROUND II
METHOD 2, GC-UV for 14 PNA's

 $\mu\text{g}/\text{m}^3$ [illegible]

B-28

TABLE IX

 HI-VOLS, ROUND I
 METHODS 1, 3, and 4

Filter No.	Co.#	mg/m ³ #1 B.S.	µg/m ³ #3 BaP	Pyr	Flu	BaA	Chr	BeP	Pery	BkF	Ant	BaP
GFA-494	D-1	1.562	12.65	20.07	47.94	13.94	6.69	2.73	2.12	3.29	1.71	26.20
GFA-493	D-5	2.864	22.99	35.50	68.58	52.44	20.17	9.28	4.44	14.92	N.D.	56.47
GFA-492	D-4	0.982	7.93	10.99	17.67	9.82	5.50	2.51	1.06	3.26	N.D.	12.56
GFA-491	D-6	0.778	8.83	5.84	8.56	12.06	6.23	2.92	1.63	5.45	N.D.	12.45
GFA-490	D-10	0.862	8.23	10.34	24.56	9.91	4.22	2.37	1.34	2.24	0.86	17.66
GFA-488	D-9	5.700	8.55	74.10	170.99	51.30	27.93	11.11	5.41	11.97	2.79	79.79
GFA-487	D-2	3.194	15.46	39.16	56.67	49.46	19.58	9.27	5.10	6.70	1.44	41.22
GFA-486	D-3	0.370	4.85	2.55	4.93	4.93	2.30	1.15	0.53	1.44	0.18	5.75
GFA-485	D-7	4.363	39.06	54.36	128.76	27.90	15.02	7.87	5.58	8.58	4.29	56.51
GFA-483	D-12	4.903	70.67	176.68	375.44	92.76	33.57	20.32	10.16	32.24	4.42	97.17
GFA-482	D-11	3.526	42.87	80.13	168.27	56.09	28.85	12.42	8.01	13.62	4.01	92.15
GFA-415	D-8	2.125	39.01	47.57	107.83	44.40	24.42	10.15	6.98	13.64	1.46	44.40
H-1	A-2	0.442	4.78	2.94	6.38	9.81	5.40	3.88	1.67	4.56	0.78	11.78
H-2	A-3	0.647	7.52	0.40	6.47	11.45	6.47	3.83	1.64	5.97	0.70	7.47
H-3	A-1	1.016	18.40	13.90	30.48	15.51	9.63	4.81	2.25	6.95	0.75	13.37
H-4	A-4	0.345	5.64	7.76	18.53	7.32	3.88	2.33	0.99	3.10	0.82	2.97
H-5	A-5	1.124	14.03	31.58	8.03	25.16	10.71	7.49	3.10	11.24	0.70	24.09
H-6	A-6	1.066	15.70	37.02	84.13	22.99	10.66	6.73	4.26	3.87	1.35	24.68
H-7	A-8	0.681	7.11	11.49	24.27	11.49	5.11	3.28	1.28	3.83	0.51	16.18
H-8	A-7	0.734	6.98	15.14	31.67	13.77	5.05	3.81	1.42	3.35	0.83	21.57
H-9	A-9	0.819	9.91	17.23	37.48	14.65	5.60	3.49	1.64	4.05	0.65	21.97
H-10	A-12	0.245	2.05	3.73	6.87	3.43	1.67	1.13	0.43	1.23	0.16	4.17
H-11	A-10	0.697	7.57	11.45	39.32	11.95	4.98	3.63	1.69	4.43	0.37	13.94
H-12	A-11	0.151	1.06	0.66	1.36	2.02	1.06	0.76	0.38	1.06	0.07	2.62
GFA-416	B-11	1.636	35.11	88.83	229.08	51.43	16.83	14.02	9.35	22.44	6.54	65.45
GFA-417	B-12	2.214	34.53	40.04	70.66	22.14	10.36	5.65	3.77	7.07	2.73	32.97
GFA-418	B	4.594	44.70	123.68	265.02	73.32	28.27	15.02	9.72	14.13	6.18	106.01
GFA-419	B	1.034	13.40	21.11	47.39	8.19	4.05	2.15	1.08	3.27	N.D.	13.79
H-13	B-1	1.802	13.41	41.82	93.73	19.47	9.37	5.55	3.17	7.93	0.18	28.84
H-14	B-2	1.356	18.00	8.63	16.84	5.34	2.59	3.49	2.79	10.68	0.30	22.19
H-15	B-3	1.094	11.74	25.66	50.48	19.35	9.68	3.24	1.22	7.99	N.D.	12.62
H-16	B-6	2.233	20.00	75.35	148.84	38.14	19.53	11.16	5.67	18.60	0.81	26.98
H-17	B-5	4.508	32.80	217.39	378.07	83.18	43.48	24.57	20.79	17.01	14.18	113.42

B-29

HI-VOLS, ROUND I
METHODS 1, 3, and 4

6-20

TABLE X

HI-VOLS, ROUND II
METHODS 1, 3, and 4

Filter No.	Co.#	mg/m ³ #1 B.S.	µg/m ³ #3 BaP	Pyr	Flu	BaA	Chr	BeP	Pery	BkF	Ant	BaP
#4 - µg/m ³												
H-60	A-23	0.340	3.35	5.52	9.34	3.44	2.50	1.40	0.64	1.49	0.02	3.78
H-61	A-21	1.016	10.21	16.58	27.27	11.23	7.49	4.17	1.12	2.30	0.20	11.23
H-62	A-22	1.076	11.42	23.05	42.00	11.78	7.68	4.92	1.95	4.40	1.18	16.39
H-63	A-26	0.493	5.57	8.87	11.34	7.39	5.91	2.56	0.84	2.61	0.36	6.90
H-64	A-24	0.863	8.53	13.70	20.81	9.14	6.09	3.50	1.37	2.34	0.38	8.12
H-66	A-25	1.634	11.97	32.47	44.50	11.42	10.22	5.05	1.98	4.99	0.96	17.54
H-67	A-29	0.722	9.61	18.06	36.84	11.56	8.67	4.12	1.66	3.54	0.80	11.56
H-68	A-28	0.555	7.31	14.81	28.24	7.41	5.09	3.06	1.06	2.82	0.56	8.80
H-69	A-27	0.589	6.87	25.51	32.38	10.79	5.89	3.29	1.18	3.09	0.59	8.34
H-73	A-32	0.641	10.54	17.24	36.46	8.87	5.42	3.94	1.28	2.71	0.89	9.85
H-74	A-31	1.234	6.32	20.23	38.49	14.80	7.90	4.34	1.58	2.42	1.04	13.32
H-75	A-30	1.198	14.54	22.32	43.01	16.33	7.08	5.01	2.01	4.03	1.20	16.33
H-80	B-22	4.306	30.81	56.46	91.87	35.41	25.84	13.40	5.36	12.44	3.92	25.84
H-81	B-23	4.884	23.38	60.68	106.56	32.56	25.16	11.54	4.88	7.40	3.55	26.64
H-82	B-21	4.285	42.85	110.59	207.35	64.28	38.01	15.90	7.60	20.74	5.60	55.29
H-83	B-26	0.289	0.99	4.13	7.85	2.40	2.23	0.70	0.27	0.45	0.20	2.69
H-84	B-25	0.398	2.83	6.97	10.46	4.13	2.99	1.54	0.65	1.64	0.60	3.49
H-85	B-24	0.393	1.84	4.28	7.38	2.90	2.02	0.84	0.38	0.64	0.21	2.80
H-86	B-27	6.943	66.95	136.38	247.97	78.11	43.40	22.32	11.28	22.32	8.93	74.39
H-87	B-28	3.364	24.05	85.90	100.21	32.21	22.91	12.17	5.44	16.46	5.30	30.06
H-88	B-29	3.873	30.26	65.78	116.93	38.73	22.66	10.23	4.02	10.23	3.14	27.04
H-89	B-31	1.825	22.44	18.85	29.80	22.50	17.03	9.73	3.59	6.69	2.98	15.81
H-90	B-32	7.548	76.97	193.09	368.63	96.55	77.24	30.72	16.68	16.68	9.66	71.97
H-91	B-30	5.250	74.81	139.46	278.91	80.39	56.60	30.35	13.12	33.63	15.59	64.81
H-94	Blank	4.000	0.04	2.20	1.90	1.40	N.E.	N.D.	N.D.	N.D.	N.D.	3.20
GFA-524	C-29	3.883	99.71	34.41	114.71	52.94	27.35	13.24	4.94	22.94	0.85	37.94
GFA-525	C-28	1.524	14.63	26.57	65.33	25.26	15.68	5.66	2.40	9.15	N.D.	16.98
GFA-526	C-27	1.269	10.25	18.81	39.02	11.28	6.58	3.76	2.35	3.48	1.03	17.87
GFA-527	C-26	1.257	14.59	19.70	46.11	27.25	15.09	10.48	6.29	10.06	1.64	34.79
GFA-528	C-24	0.578	4.75	0.44	N.D.	4.22	3.15	1.73	0.62	2.75	N.D.	3.20
GFA-529	C-25	0.879	12.10	20.51	62.80	17.16	9.21	6.28	4.19	7.95	1.30	14.65
GFA-530	C-23	0.488	4.56	16.84	33.68	7.09	3.94	3.10	2.35	0.75	1.51	12.41
GFA-531	C-21	1.391	9.53	51.51	128.77	18.54	11.33	8.24	6.18	10.30	4.02	29.88

TABLE X

 HI-VOLS, ROUND II
 METHODS 1, 3, and 4

Filter No.	Co.#	mg/m ³ #1 B.S.	µg/m ³ #3 BaP	Pyr	Flu	BaA	Chr	BeP	Pery	BkF	Ant	BaP
GFA-532	C-22	0.311	2.34	1.20	2.98	4.45	2.67	1.16	0.89	1.78	0.35	7.12
GFA-533	C-32	1.685	10.99	28.38	74.48	14.19	7.54	3.81	2.48	4.34	1.24	23.94
GFA-534	C-30	3.396	21.48	110.37	322.62	61.13	30.56	15.28	11.89	18.68	6.54	59.43
GFA-535	C-31	2.019	14.32	74.34	192.74	33.96	16.52	12.85	8.54	7.25	6.79	62.41
GFA-536	Blank	2.000	2.30									
H-22	D-23	2.907	52.63	40.10	75.19	25.06	12.03	7.02	5.01	4.66	2.96	60.15
H-23	D-22	29.49	384.35	794.12	1800.00	529.41	148.24	95.29	58.24	68.82	25.94	688.24
H-24	D-21	6.279	106.25	122.27	264.38	71.05	33.05	18.18	19.83	16.52	7.10	130.54
H-25	D-24	5.214	60.10	98.80	192.12	49.40	20.31	17.56	15.92	15.37	7.14	96.06
H-26	D-25	22.95	335.52	878.87	1706.04	346.38	170.60	82.72	67.21	98.23	25.85	620.38
H-27	D-26	7.002	41.50	131.29	226.11	80.23	37.93	15.32	13.13	13.13	6.42	145.88
H-28	D-28	8.885	78.69	196.73	310.96	114.23	51.40	23.48	12.06	24.12	8.25	139.62
H-29	D-29	10.67	87.26	201.92	418.26	151.44	65.62	31.01	20.91	37.50	7.21	165.86
H-30	D-27	4.460	41.03	55.78	92.97	29.13	12.40	9.30	14.88	7.44	3.78	61.98
H-32	D-30	3.350	32.25	75.75	135.26	31.92	16.77	11.36	7.03	16.23	2.70	59.52
H-33	D-31	2.870	24.03	89.35	225.73	36.68	16.45	7.99	6.58	12.23	2.68	40.44
H-36	D-32	6.210	59.88	194.58	477.04	106.71	38.92	25.74	14.44	49.59	5.71	100.43
H-42	E-30	0.720	17.49	4.42	3.91	12.86	12.86	6.69	3.09	6.17	3.40	13.89
H-43	E-31	0.638	14.29	8.50	10.63	14.35	5.84	3.72	2.39	4.41	1.01	7.97
H-44	E-32	0.834	15.28	10.43	13.04	12.52	12.00	5.22	2.40	5.22	2.76	17.73
H-45	E-27	12.250	148.41	216.73	315.66	113.07	117.79	56.54	24.50	42.40	25.44	207.30
H-46	E-28	1.593	21.96	37.65	62.75	26.07	24.62	8.69	4.78	12.55	3.43	38.14
H-47	E-29	0.550	9.35	13.74	21.53	9.62	8.70	4.03	2.02	4.22	1.79	12.83
H-48	E-23	0.297	0.608	5.42	8.16	5.04	3.26	1.78	1.04	2.60	0.82	6.16
H-49	E-21	0.213	1.53	1.70	2.41	2.70	2.06	1.21	0.54	1.56	0.41	4.33
H-50	E-22	1.043	11.23	15.24	23.26	16.85	10.43	4.25	3.29	6.90	1.60	20.86
H-51	E-25	0.882	7.27	14.29	21.85	13.87	10.08	3.87	2.73	5.46	1.72	15.13
H-52	E-26	0.790	9.40	39.11	71.11	16.59	11.85	5.14	3.75	5.53	3.48	19.36
H-53	E-24	0.235	0.62	5.88	9.02	4.31	2.94	1.14	0.82	1.57	0.55	4.71

TABLE XI

Hi-Vols, Round I
Method 6, Metals

$\mu\text{g}/\text{m}^3$							
Filter No.	Co.#	Co	Cr	Cu	Mn	Ni	Zn
H-1	A-2	<0.02	0.24	0.34	2.43	0.08	2.58
H-2	A-3	<0.02	0.23	0.82	2.43	0.20	4.05
H-3	A-1	0.05	0.09	0.64	1.09	0.05	6.70
H-4	A-4	<0.11	0.10	0.34	0.98	0.10	2.00
H-5	A-5	<0.03	0.15	0.65	1.04	0.13	6.86
H-6	A-6	<0.03	0.20	0.63	1.21	0.12	7.71
H-7	A-8	<0.02	0.14	0.65	0.77	0.12	8.30
H-8	A-7	<0.02	0.12	0.60	0.68	0.10	8.95
H-9	A-9	<0.02	0.12	0.24	0.57	0.07	4.09
H-10	A-12	<0.02	0.12	0.64	0.71	0.12	7.16
H-11	A-10	<0.02	0.18	0.64	1.12	0.10	6.80
H-12	A-11	<0.03	0.10	0.35	0.75	0.17	3.42
GFA-416	B-11	<0.02	0.21	1.30	1.44	0.12	3.92
GFA-417	B-12	<0.02	0.22	0.54	1.33	0.14	5.09
GFA-418	B	<0.04	0.39	3.78	2.23	0.25	7.01
GFA-419	B	<0.02	0.20	0.59	0.74	0.06	3.26
H-13	B-1	<0.04	0.23	4.00	1.82	0.26	5.66
H-14	B-2	<0.02	0.22	0.57	2.28	0.22	2.80
H-15	B-3	<0.02	0.24	0.94	2.49	0.25	4.38
H-16	B-6	<0.05	0.45	1.07	1.39	0.15	11.16
H-17	B-5	<0.05	<0.05	0.49	1.27	0.16	7.11
H-18	B-4	<0.03	0.54	4.68	2.95	0.32	6.83
H-19	B-8	<0.05	<0.05	2.71	0.86	0.11	6.86
H-20	B-9	<0.02	0.05	0.30	0.87	0.09	7.66
GFA-481	C-10	0.04	0.16	1.12	2.91	0.16	3.45
GFA-480	C-11	<0.02	0.14	0.29	1.07	0.09	7.11
GFA-479	C-12	<0.03	0.15	0.35	1.03	0.11	8.16
GFA-478	C-7	0.04	0.14	0.36	1.04	0.10	3.25
GFA-477	C-9	0.03	0.34	1.08	1.66	0.38	23.20
GFA-476	C-8	<0.03	0.27	0.61	1.44	0.19	11.72
GFA-475	C-5	<0.02	0.03	0.59	6.02	0.15	11.36
GFA-474	C-6	<0.02	0.10	0.66	5.19	0.11	21.68
GFA-473	C-4	0.03	0.18	0.35	6.36	0.14	8.99
GFA-472	C-1	<0.02	0.35	1.06	5.20	0.21	54.43
GFA-471	C-3	<0.02	0.42	0.98	4.76	0.09	77.16
GFA-470	C-2	<0.02	0.45	0.68	4.97	0.12	79.13
GFA-494	D-1	<0.03	0.30	1.59	2.07	0.67	3.59
GFA-493	D-5	<0.02	0.19	2.60	4.58	0.14	7.32
GFA-492	D-4	<0.02	0.17	1.23	1.20	0.05	4.75
GFA-491	D-6	<0.02	0.10	0.63	1.49	0.03	4.13
GFA-490	D-10	<0.02	0.20	1.35	0.98	0.09	5.92
GFA-488	D-9	<0.01	0.18	1.10	3.98	0.21	5.46
GFA-487	D-2	<0.02	0.19	0.91	2.69	0.16	6.80

TABLE XI

Hi-Vols, Round I
Method 6, Metals

$\mu\text{g}/\text{m}^3$							
Filter No.	Co.#	Co	Cr	Cu	Mn	Ni	Zn
GFA-486	D-3	<0.02	0.17	0.46	1.84	0.11	3.02
GFA-485	D-7	<0.04	0.26	1.52	2.32	0.15	7.12
GFA-483	D-12	<0.02	0.13	0.62	1.17	0.08	3.15
GFA-482	D-11	<0.02	0.10	0.41	0.68	0.08	10.88
GFA-415	D-8	<0.02	0.11	0.83	1.58	0.06	4.57
GFA-495	E-3	0.02	0.11	0.79	0.69	0.09	3.76
GFA-496	E-2	<0.02	0.14	1.70	1.98	0.05	3.73
GFA-497	E-1	0.07	0.11	0.84	0.89	0.12	2.51
GFA-498	E-4	<0.020	0.11	0.40	3.73	0.06	2.70
GFA-499	E-5	<0.02	0.15	0.68	4.68	0.07	3.71
GFA-500	E-6	<0.02	0.13	0.95	5.59	0.08	3.83
GFA-501	E-11	<0.02	0.16	0.52	1.48	0.04	1.94
GFA-502	E-12	<0.02	0.14	0.79	1.40	0.05	2.22
GFA-503	E-9	<0.02	0.10	0.71	2.14	0.06	3.19
GFA-504	E-8	<0.02	0.08	0.37	1.44	0.05	1.48
GFA-505	E-7	<0.02	0.09	0.74	1.27	0.05	1.42
GFA-506	E-10	<0.02	0.14	0.33	1.23	0.05	1.51

TABLE XII

Hi-Vols, Round II
Method 6, Metals

$\mu\text{g}/\text{m}^3$

Filter No.	Co.#	Co	Cr	Cu	Mn	Ni	Zn
H-60	A-23	0.059	0.187	0.38	0.22	0.10	2.84
H-61	A-21	<0.03	0.21	0.72	0.83	0.13	5.78
H-62	A-22	<0.03	0.27	0.32	0.66	0.21	6.13
H-63	A-26	0.03	0.17	0.20	0.15	0.09	3.75
H-64	A-24	0.02	0.41	0.27	0.74	0.12	7.63
H-66	A-25	0.03	0.36	1.28	0.76	0.13	9.48
H-67	A-29	0.04	0.80	0.67	0.27	0.23	4.69
H-68	A-28	0.02	0.53	0.50	0.41	0.17	5.26
H-69	A-27	0.02	0.54	0.37	0.38	0.18	5.62
H-73	A-32	0.02	0.66	0.82	0.37	0.207	5.49
H-74	A-31	<0.02	0.40	0.36	0.93	0.12	2.89
H-75	A-30	<0.03	0.67	0.47	1.11	0.17	4.04
H-80	B-22	<0.05	0.26	0.63	2.35	0.28	9.19
H-81	B-23	<0.07	0.46	1.95	2.86	0.33	9.99
H-82	B-21	<0.03	0.52	1.38	1.61	0.17	4.26
H-83	B-26	<0.02	0.49	1.11	1.78	0.13	2.77
H-84	B-25	<0.02	0.59	0.53	1.87	0.16	3.53
H-85	B-24	<0.02	0.57	1.17	1.97	0.14	2.14
H-86	B-27	<0.06	0.68	1.60	1.72	0.24	10.94
H-87	B-28	0.04	0.36	0.39	0.58	0.14	18.50
H-88	B-29	<0.04	0.40	1.69	0.83	0.15	7.97
H-89	B-31	<0.03	0.22	0.54	1.68	0.19	5.99
H-90	B-32	<0.04	0.24	1.37	1.82	0.18	7.52
H-91	B-30	<0.04	0.22	1.21	1.28	0.16	4.80
GFA-524	C-29	0.06	0.22	0.71	2.20	0.24	20.53
GFA-525	C-28	<0.02	0.30	1.08	2.47	0.31	10.52
GFA-526	C-27	<0.02	0.30	0.97	2.01	0.23	6.09
GFA-527	C-26	<0.02	0.84	0.57	3.25	0.21	44.59
GFA-528	C-24	0.02	0.60	1.28	3.62	0.36	9.12
GFA-529	C-25	<0.02	0.23	0.53	2.45	0.22	10.60
GFA-530	C-23	<0.02	1.15	0.47	2.56	0.12	14.84
GFA-531	C-21	<0.03	1.20	1.38	3.51	0.36	24.28
GFA-532	C-22	<0.02	1.36	0.87	2.38	0.13	14.80
GFA-533	C-32	<0.04	0.32	1.07	3.48	0.20	23.02
GFA-534	C-30	<0.04	0.43	1.85	5.20	0.26	16.54
GFA-535	C-31	<0.05	0.34	1.18	3.74	0.34	18.27
H-22	D-23	<0.02	0.12	0.85	5.13	0.12	16.25
H-23	D-22	<0.03	0.14	1.11	9.54	0.24	14.51
H-24	D-21	<0.08	0.35	1.22	5.95	0.20	13.04
H-25	D-24	<0.14	0.63	1.48	1.56	0.30	26.04
H-26	D-25	<0.03	0.14	1.26	2.78	0.14	8.44
H-27	D-26	<0.04	0.20	1.34	2.59	0.12	17.94
H-28	D-28	<0.03	0.25	0.62	12.17	0.40	28.75

TABLE XII

Hi-Vols, Round II
Method 6, Metals

$\mu\text{g}/\text{m}^3$							
Filter No.	Co.#	Co	Cr	Cu	Mn	Ni	Zn
H-29	D-29	<0.04	0.27	0.71	9.02	0.19	27.86
H-30	D-27	0.03	0.28	0.55	8.58	0.20	25.34
H-32	D-30	<0.03	0.28	0.49	1.14	0.14	8.94
H-33	D-31	<0.02	0.14	0.42	0.61	0.07	2.76
H-36	D-32	<0.03	0.23	0.69	0.67	1.41	5.49
H-42	E-30	<0.03	0.44	0.96	1.92	0.18	7.60
H-43	E-31	<0.03	0.303	0.52	2.09	0.17	8.18
H-44	E-32	<0.03	1.23	0.89	3.35	0.22	9.51
H-45	E-27	<0.24	3.16	4.10	8.90	0.71	68.64
H-46	E-28	<0.02	0.59	0.59	2.21	0.16	8.28
H-47	E-29	<0.02	0.52	1.44	3.05	0.15	7.53
H-48	E-23	0.04	0.48	0.48	2.55	0.24	7.17
H-49	E-21	<0.04	0.50	1.41	3.41	0.33	7.38
H-50	E-22	<0.04	0.59	2.71	3.22	0.22	12.39
H-51	E-25	0.02	0.29	0.60	3.14	0.15	16.89
H-52	E-26	<0.02	0.33	0.35	2.88	0.19	12.51
H-53	E-24	<0.02	0.38	0.97	3.66	0.27	18.27

TABLE XIII

HI-VOLS, ROUND I
METHOD 2 - GC-UV for 14 PNA's

$\mu\text{g}/\text{m}^3$

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBehA	BghiP	Ant
H-1	A-2	3.43	2.65	0.74	7.36	9.81	N.D.	5.89	0.93	3.24	4.12	7.36	N.D.	3.58	0.79
H-2	A-3	4.83	3.29	0.75	6.47	7.96	N.D.	1.79	0.55	1.14	3.98	6.97	N.D.	4.03	1.14
H-3	A-1	6.95	3.21	0.64	5.88	6.95	N.D.	2.83	0.75	1.93	2.57	6.15	0.50	2.46	0.64
H-4	A-4	6.03	4.05	33.61	1.16	1.68	N.D.	2.11	0.52	1.59	1.90	3.71	N.D.	1.29	0.21
H-5	A-5	23.02	19.81	1.34	10.71	19.27	N.D.	7.50	1.71	4.93	6.96	13.92	N.D.	5.14	1.29
H-6	A-6	23.56	20.19	1.12	5.61	10.66	N.D.	33.65	1.36	4.09	4.82	10.10	N.D.	5.61	1.51
H-7	A-8	10.64	8.51	0.81	6.81	9.37	N.D.	3.75	1.24	2.90	3.49	3.45	N.D.	3.66	0.81
H-8	A-7	5.51	4.13	0.35	2.20	3.30	N.D.	0.83	0.15	0.92	0.87	1.79	N.D.	0.78	N.D.
H-9	A-9	6.89	6.89	0.40	2.89	5.17	N.D.	0.91	0.52	1.08	0.86	2.20	N.D.	0.86	0.17
H-10	A-12	1.91	1.47	0.40	0.64	0.88	N.D.	1.28	0.30	0.74	0.98	1.72	N.D.	0.79	0.13
H-11	A-10	11.45	8.46	0.50	7.47	9.96	N.D.	4.73	1.00	2.84	4.13	7.97	0.43	2.24	0.38
H-12	A-11	1.36	1.06	N.D.	1.21	1.41	N.D.	1.11	0.35	0.86	0.76	3.03	N.D.	1.82	0.23
GFA-416	B-11	28.52	22.44	1.17	10.29	16.83	N.D.	7.01	2.01	5.61	3.79	13.56	N.D.	5.14	2.29
GFA-417	B-12	70.65	45.69	2.54	23.55	39.10	N.D.	17.90	3.63	11.30	11.30	30.15	N.D.	13.66	6.59
GFA-418	B	512.37	388.69	N.D.	176.68	256.18	N.D.	83.92	20.32	71.55	69.79	29.15	8.83	61.84	28.27
GFA-419	B	1.68	5.17	N.D.	6.46	14.65	N.D.	N.D.	N.D.	N.D.	0.40	1.68	N.D.	N.D.	N.D.
H-13	B-1	26.68	22.35	N.D.	7.07	12.26	N.D.	6.78	1.66	3.24	3.75	13.70	N.D.	5.05	2.45
H-14	B-2	13.15	13.15	0.99	7.40	14.38	N.D.	3.12	2.30	3.25	2.18	8.22	4.52	4.93	1.81
H-15	B-3	11.78	13.88	N.D.	7.57	13.04	N.D.	4.08	1.30	3.74	3.87	10.52	0.46	3.53	1.30
H-16	B-6	17.67	66.05	3.44	26.05	41.86	N.D.	17.67	3.53	12.09	13.95	36.28	N.D.	19.53	8.56
H-17	B-5	160.68	132.33	5.39	49.15	75.61	N.D.	36.86	8.60	20.79	9.45	17.96	N.D.	36.86	16.07
H-18	B-4	9.70	10.40	N.D.	9.01	13.17	N.D.	6.58	1.80	5.68	5.13	13.86	2.84	6.93	1.11
H-19	B-8	87.90	94.52	3.50	26.47	42.53	N.D.	13.23	4.82	11.34	13.23	37.81	2.74	19.85	10.40
H-20	B-9	18.37	15.07	1.46	12.25	19.31	N.D.	9.42	2.68	6.59	7.54	20.73	3.01	9.42	4.52
GFA-470	C-2	5.58	4.32	N.D.	4.51	6.51	N.D.	3.81	0.79	2.37	2.65	5.58	N.D.	2.84	0.79
GFA-471	C-3	7.07	4.71	0.61	4.10	7.07	N.D.	5.65	1.04	2.59	2.59	5.65	0.80	2.68	0.80
GFA-472	C-1	9.89	9.89	1.13	10.36	14.60	N.D.	9.89	3.25	4.15	4.15	9.89	N.D.	6.12	2.07
GFA-473	C-4	1.88	1.65	N.D.	2.63	2.91	N.D.	1.22	0.36	1.18	1.18	3.69	N.D.	0.71	0.22
GFA-474	C-6	15.08	12.06	0.99	8.62	11.63	N.D.	6.03	1.16	23.70	1.21	2.80	N.D.	3.66	1.55
GFA-475	C-5	29.20	17.43	2.40	10.83	16.49	N.D.	8.95	1.84	5.65	5.65	13.66	0.89	5.65	1.88
GFA-476	C-8	3.32	2.98	0.38	1.22	1.60	N.D.	2.16	0.46	1.22	1.44	2.98	0.94	1.27	0.45
GFA-477	C-9	5.70	4.90	1.03	6.84	5.70	N.D.	4.27	0.74	2.79	2.74	5.41	1.20	3.08	0.68
GFA-478	C-7	15.70	13.34	3.85	24.33	32.18	N.D.	16.48	3.06	10.20	12.56	23.55	N.D.	10.20	2.20

6-37

TABLE XIII

HI-VOLS, ROUND I
METHOD 2 - GC-UV for 14 PNA's

µg/m³

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBahA	BghiP	Ant
GFA-479	C-12	4.97	2.65	0.18	2.21	3.32	N.D.	0.99	0.44	0.77	1.11	2.38	0.43	0.94	0.34
GFA-480	C-11	5.97	4.59	0.64	3.81	5.05	N.D.	2.52	0.73	0.73	N.D.	N.D.	N.D.	1.24	0.51
GFA-481	C-10	1.77	2.02	N.D.	1.98	2.63	N.D.	1.29	0.38	0.95	0.78	2.67	0.25	0.99	0.28
GFA-415	D-8	30.13	25.69	3.17	16.81	28.23	N.D.	12.05	3.81	8.25	9.20	21.88	23.79	8.25	2.76
GFA-482	D-11	36.06	38.46	3.81	24.84	37.66	N.D.	10.42	2.72	9.62	34.86	88.14	N.D.	8.41	3.41
GFA-483	D-12	21.20	37.99	2.96	8.83	17.67	N.D.	3.58	0.97	2.47	2.34	5.74	N.D.	6.18	2.61
GFA-485	D-7	36.48	31.47	1.50	13.59	18.60	N.D.	6.44	2.58	5.51	7.87	17.88	N.D.	7.87	4.08
GFA-486	D-3	1.32	1.11	N.D.	1.07	1.56	N.D.	0.66	0.13	0.62	0.74	1.48	N.D.	N.D.	N.D.
GFA-487	D-2	19.58	22.15	1.29	21.64	31.94	N.D.	6.18	3.30	8.24	8.24	10.30	2.42	5.67	2.37
GFA-488	D-9	2.74	10.83	2.11	22.23	39.90	N.D.	7.98	3.14	8.55	8.83	24.79	N.D.	8.26	3.42
GFA-490	D-10	4.05	3.23	0.32	2.67	3.58	N.D.	1.12	0.35	0.78	1.38	3.19	N.D.	1.25	0.41
GFA-491	D-6	3.27	2.84	0.89	4.67	5.84	N.D.	3.11	1.32	2.84	2.26	6.23	N.D.	2.41	0.74
GFA-492	D-4	5.50	5.50	0.51	3.42	5.50	N.D.	2.12	0.90	2.08	1.85	4.71	0.67	2.32	0.79
GFA-493	D-5	27.43	N.D.	5.24	18.56	33.08	N.D.	14.93	5.65	11.70	8.47	20.98	N.D.	7.66	2.38
GFA-494	D-1	10.59	8.36	0.84	6.69	13.94	N.D.	2.40	1.62	4.24	1.90	7.80	1.39	3.23	1.00
GFA-495	E-3	31.46	21.78	1.99	14.52	21.30	N.D.	9.20	3.87	7.26	8.71	22.75	9.20	5.81	2.42
GFA-496	E-2	4.22	4.51	0.64	5.40	6.38	N.D.	1.91	1.33	2.06	1.82	4.91	3.43	1.82	0.74
GFA-497	E-1	85.19	20.81	4.84	42.11	55.66	N.D.	19.85	5.32	25.17	15.01	44.53	N.D.	17.43	10.17
GFA-498	E-4	112.02	116.33	4.74	32.31	64.63	N.D.	249.89	15.51	21.11	15.51	20.25	N.D.	27.57	0.86
GFA-499	E-5	33.60	32.72	2.05	20.07	24.87	N.D.	12.22	2.14	9.16	7.42	21.38	2.18	9.16	4.36
GFA-500	E-6	7.19	7.19	0.63	8.99	9.89	N.D.	2.70	0.72	2.02	1.66	5.85	1.08	1.66	0.94
GFA-501	E-11	2.50	3.50	0.70	0.90	2.00	N.D.	3.30	2.85	1.00	N.D.	N.D.	N.D.	2.20	0.85
GFA-502	E-12	2.66	2.32	0.25	3.15	4.16	N.D.	0.28	0.23	0.46	1.26	3.15	0.58	1.07	0.58
GFA-503	E-9	18.90	15.82	6.15	15.82	22.86	N.D.	7.03	2.55	5.28	0.75	1.14	N.D.	N.D.	N.D.
GFA-504	E-8	26.71	19.39	N.D.	13.36	2.07	N.D.	2.67	2.03	3.49	5.60	11.63	N.D.	4.05	1.64
GFA-505	E-7	12.35	9.79	N.D.	1.19	1.96	N.D.	0.13	0.29	1.19	1.96	5.11	N.D.	1.45	0.68
GFA-506	E-10	6.58	6.58	0.47	5.17	7.05	N.D.	10.81	10.34	3.76	2.02	2.35	0.66	1.41	0.80

B-38

TABLE XIV

HI-VOLS, ROUND II
METHOD 2 - GC-UV for 14 PNA's

$\mu\text{g}/\text{m}^3$

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBaH	BghP	Ant
H-60	A-23	4.03	3.69	N.D.	2.59	3.61	N.D.	1.44	0.64	1.32	1.57	5.52	N.D.	2.16	0.51
H-61	A-21	14.44	17.11	N.D.	9.62	15.51	N.D.	4.54	1.71	4.17	4.60	11.23	N.D.	2.89	1.12
H-62	A-22	14.85	10.24	1.18	3.89	4.05	N.D.	3.13	0.87	2.30	3.23	7.17	1.18	1.18	0.82
H-63	A-26	6.41	9.86	0.23	5.42	25.13	N.D.	3.45	0.89	2.71	3.06	6.41	0.79	2.27	0.54
H-64	A-24	21.82	15.73	0.56	5.08	9.14	N.D.	1.32	2.74	0.61	1.37	5.08	0.86	3.20	1.07
H-66	A-25	28.26	20.44	1.32	12.03	16.24	N.D.	4.87	1.92	4.03	4.51	10.82	1.50	2.10	0.66
H-67	A-29	18.78	14.45	0.59	8.67	13.00	N.D.	5.71	0.64	4.77	4.04	7.95	0.72	4.12	1.08
H-68	A-28	13.42	9.72	0.74	5.55	7.87	N.D.	3.56	1.02	2.45	2.27	6.02	0.56	2.59	0.65
H-69	A-27	17.17	11.77	N.D.	5.40	8.83	N.D.	3.43	1.18	2.70	2.50	5.40	0.64	0.98	0.36
H-73	A-32	20.69	14.29	1.04	5.91	10.36	N.D.	3.01	2.56	3.20	2.07	5.91	0.54	3.06	0.94
H-74	A-31	19.25	14.80	N.D.	8.39	13.82	N.D.	3.40	2.32	3.40	1.73	5.43	1.48	3.01	0.79
H-75	A-30	16.88	14.16	0.65	5.34	9.26	N.D.	2.94	0.98	2.34	2.88	6.53	1.42	2.88	0.98
H-80	B-22	60.29	46.89	N.D.	15.31	28.71	N.D.	6.60	2.20	7.27	8.33	23.92	6.12	5.84	3.54
H-81	B-23	69.56	51.80	N.D.	19.24	39.96	N.D.	9.18	3.55	8.44	7.40	20.72	6.96	10.36	3.70
H-82	B-21	96.76	64.97	3.94	26.26	40.09	N.D.	14.51	4.15	11.75	12.44	31.10	1.73	12.44	5.67
H-83	B-26	3.22	2.56	0.16	1.45	2.02	N.D.	0.54	0.18	0.41	0.54	1.32	0.27	0.50	0.22
H-84	B-25	4.98	4.63	N.D.	1.89	3.19	N.D.	1.14	0.40	0.90	1.05	2.09	N.D.	N.D.	N.D.
H-85	B-24	3.89	3.05	0.22	1.67	2.41	N.D.	0.74	0.21	0.54	0.79	1.72	0.54	N.D.	0.34
H-86	B-27	76.87	54.55	4.09	19.84	24.80	N.D.	8.56	3.84	8.31	8.93	24.80	6.70	4.09	4.09
H-87	B-28	33.64	33.64	0.78	10.74	16.46	N.D.	6.16	1.72	4.51	5.44	15.03	1.58	9.30	3.44
H-88	B-29	47.50	35.08	3.22	16.08	22.66	N.D.	1.90	0.53	1.83	7.02	18.27	1.46	7.09	2.78
H-89	B-31	26.76	19.46	9.73	13.38	20.68	N.D.	6.69	1.70	5.84	5.29	15.20	1.95	8.52	3.47
H-90	B-32	122.88	87.77	3.60	20.19	43.01	N.D.	13.16	6.85	12.29	10.53	34.23	1.76	16.68	7.55
H-91	B-30	131.25	98.44	1.97	36.09	73.83	N.D.	30.35	9.84	20.51	14.77	43.48	3.61	10.66	5.58
H-94	Blank	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GFA-524	C-29	62.65	36.18	3.71	22.94	35.30	N.D.	23.82	6.35	16.77	19.41	45.00	N.D.	12.35	7.32
GFA-525	C-28	60.97	43.55	2.26	20.03	25.26	N.D.	6.97	1.39	4.36	6.32	13.94	0.78	10.45	5.23
GFA-526	C-27	21.16	16.93	1.46	7.52	9.40	N.D.	5.17	1.03	3.34	3.95	8.93	N.D.	5.17	3.38
GFA-527	C-26	54.49	40.66	4.61	27.66	21.38	N.D.	7.13	1.38	4.61	13.41	30.18	3.23	14.25	5.45
GFA-528	C-24	11.11	10.66	N.D.	13.77	17.77	N.D.	5.33	4.89	7.11	2.62	4.89	N.D.	6.22	1.20
GFA-529	C-25	62.80	34.33	1.97	20.10	26.37	N.D.	20.51	3.68	10.88	35.17	79.12	2.68	13.40	5.44
GFA-530	C-23	28.37	22.60	2.30	11.08	13.74	N.D.	7.98	1.64	4.43	6.65	11.97	N.D.	8.42	2.92
GFA-531	C-21	36.06	33.48	0.67	8.76	13.91	N.D.	8.24	1.34	3.61	7.21	15.45	N.D.	8.76	3.55

B-39

TABLE XIV

HI-VOLS, ROUND II
METHOD 2 - GC-UV for 14 PNA's

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBaH	BghiP	Ant
GFA-532	C-22	1.47	1.02	0.67	2.36	3.20	N.D.	3.07	0.43	1.20	1.51	3.96	N.D.	1.47	0.42
GFA-533	C-32	74.48	43.45	2.39	21.28	31.04	N.D.	14.19	2.57	7.63	7.63	16.85	N.D.	6.21	2.66
GFA-534	C-30	118.86	68.77	3.74	41.60	61.13	N.D.	19.53	4.16	11.89	12.74	26.32	N.D.	14.43	5.86
GFA-535	C-31	82.60	48.64	1.56	19.27	24.78	N.D.	17.44	2.66	7.43	11.93	25.70	ND..	12.85	5.42
H-22	D-23	39.60	25.56	2.71	23.06	28.57	N.D.	6.52	6.52	6.52	7.52	22.06	29.07	1.50	0.70
H-23	D-22	68.82	52.94	N.D.	58.24	47.12	N.D.	58.24	33.88	79.41	23.29	49.76	4.08	24.88	12.18
H-24	D-21	110.71	46.27	4.13	36.35	21.48	N.D.	143.76	8.59	18.18	4.79	34.70	6.28	16.19	10.91
H-25	D-24	60.38	52.15	4.12	24.70	35.68	N.D.	11.80	3.57	8.51	10.16	24.43	N.D.	11.25	3.02
H-26	D-25	191.28	387.74	23.26	50.15	56.87	N.D.	29.48	72.38	25.85	15.51	44.98	3.57	14.48	5.69
H-27	D-26	80.23	167.76	8.02	35.01	47.41	N.D.	14.59	7.15	13.13	10.94	30.64	4.60	9.48	3.94
H-28	D-28	126.92	76.15	5.08	29.83	46.33	N.D.	10.79	3.68	11.42	13.96	24.12	N.D.	13.96	4.70
H-29	D-29	61.30	39.66	2.23	18.75	14.42	N.D.	25.24	5.91	19.47	4.83	12.26	1.08	6.06	1.80
H-30	D-27	42.15	36.57	2.17	13.02	21.69	N.D.	6.20	2.11	5.76	5.95	15.50	N.D.	3.60	1.49
H-32	D-30	14.07	10.28	2.33	15.15	22.18	N.D.	5.09	1.52	4.33	5.95	15.69	N.D.	6.49	2.76
H-33	D-31	15.52	31.04	5.17	18.34	29.16	N.D.	6.11	2.44	6.11	5.64	19.28	4.04	5.17	2.49
H-36	D-32	46.45	69.05	4.90	39.54	62.77	N.D.	15.06	4.27	11.93	15.06	41.43	1.19	10.67	6.03
H-42	E-30	0.39	0.67	N.D.	1.95	1.95	N.D.	1.18	0.26	0.93	1.03	2.68	N.D.	0.67	0.12
H-43	E-31	15.94	15.94	N.D.	22.32	29.22	N.D.	6.38	3.35	6.91	9.03	21.79	2.23	2.76	2.02
H-44	E-32	9.91	9.91	0.41	11.47	16.69	N.D.	5.11	5.16	1.25	5.22	14.60	0.89	6.26	3.02
H-45	E-27	150.77	164.90	3.20	75.38	122.50	N.D.	28.27	12.72	37.22	35.34	113.07	8.95	46.64	26.86
H-46	E-28	31.86	26.55	0.23	12.55	22.69	N.D.	7.72	2.51	6.76	5.31	17.86	1.40	6.76	3.04
H-47	E-29	12.83	11.45	1.28	6.87	10.08	N.D.	4.58	1.56	3.80	4.26	11.45	0.50	4.58	1.97
H-48	E-23	2.89	2.89	N.D.	1.11	1.04	N.D.	1.71	0.44	1.26	1.34	3.49	0.74	1.26	0.56
H-49	E-21	1.14	1.56	N.D.	2.62	2.77	N.D.	1.21	0.55	1.35	1.63	2.98	N.D.	1.84	0.45
H-50	E-22	8.02	7.86	1.12	8.82	11.23	N.D.	4.41	1.52	4.97	3.85	10.43	1.20	4.01	1.77
H-51	E-25	3.78	3.78	N.D.	5.46	7.14	N.D.	2.14	0.67	1.93	2.23	10.08	N.D.	2.69	1.18
H-52	E-26	27.65	20.94	0.47	11.06	15.80	N.D.	6.32	2.21	4.74	4.74	15.01	1.78	7.11	3.28
H-53	E-24	3.61	3.41	N.D.	3.18	3.53	N.D.	1.41	0.39	1.02	1.37	4.31	N.D.	1.84	0.63

B-40

TABLE XV

Personals, Round I
Methods 1 and 3

		mg/m ³		µg/m ³				mg/m ³		µg/m ³	
Filter						Filter					
No.	Co.#	#1 B.S.	#3 BaP			No.	Co.#	#1 B.S.	#3 BaP		
PS-3	A	1.017	5.378			GSG-71	B	<0.161	6.129		
PS-2	A	0.149	0.597			GSM-42	B	2.649	26.490		
PS-8	A	1.453	39.244			GSM-45	B	3.836	21.918		
PS-4	A	1.037	1.333			GSM-41,69	B	1.911	11.783		
PS-7	A	0.426	3.404			GSM-53	B	1.310	15.866		
PS-9	A	1.435	1.148			GSM-57	B	0.950	19.674		
PS-5	A	1.148	2.152			GSM-56	B	0.560	1.541		
PS-14	A	0.291				GSM-50	B		19.549		
PS-31	A	0.709	3.262			GSM-55	B	0.406	2.842		
PS-32	A	1.261	5.462			GSM-39	B	0.452	4.072		
PS-35	A	0.142	1.121			GSM-54,31	B	7.052	97.649		
PS-39,50	A	1.148	9.756			GSM-33	B	0.671	2.01		
PS-33	A	1.120	1.218			GSM-32	B	3.651	44.444		
PS-36,42	A	0.980	3.361			GSM-34	B	<0.175	7.895		
PS-41	A	0.567	1.418			GSG-78	C	2.462	19.152		
PSM-2	A	<0.137	5.753			GSG-81	C	0.754	11.614		
PS-47	A	1.370	7.808			GSG-63	C	0.294	5.147		
PS-56	A	0.685	0.438			GSG-80	C	0.415	8.299		
PS-52	A	0.420	1.681			GSG-83	C	0.420	5.462		
PSG-9	A	0.411	8.904			GSG-84	C	0.392	4.706		
PSM-8	A	0.542	6.911			GSG-89	C	0.280	2.801		
PSM-3,7	A	0.147	3.529			GSG-92	C	0.283	9.065		
PSG-5,6	A	0.530	2.473			GSG-93	C	<0.139	7.789		
PS-55	A	0.417	2.083			GSG-95	C	1.872	8.690		
PS-49	A	0.141	2.672			GSG-97	C	0.290	12.337		
PS-45	A	0.279	2.089			GSG-96	C	0.140	7.003		
PSG-1	A	<0.139	1.099			GSG-118	C	0.142	7.507		
PSG-10	A	1.127	4.085			GSG-101	C	1.000	8.286		
PS-46	A	0.143	7.174			GSG-113	C	5.495	21.978		
PSG-4	A	0.462	2.462			GSG-100	C	0.435	8.708		
GSG-43	B	6.303	10.903			GSG-102	C	<0.149	7.761		
GSG-42	B	2.410	10.843			GSM-96	C	0.452	8.145		
GSG-40	B	0.398	14.834			GSM-95	C	0.435	2.467		
GSG-45	B	3.260	32.581			GSM-99	C	0.280	8.964		
GSG-44	B	1.624	8.390			GSM-71	C	1.070	8.690		
GSG-53	B	0.824				GSM-77	C	1.550	18.088		
GSG-49	B	2.497	41.609			GSM-75	C	0.270	6.216		
GSG-52	B		6.225			GSM-73	C	0.255	1.529		
GSG-55	B	0.677	3.383			GSM-87	C	1.872	18.717		
GSG-60	B	0.789	12.145			GSM-82	C	<0.120	0.720		
GSG-56	B	0.139	6.267			GSM-78	C	0.270	10.40		
GSG-57	B	0.896	13.731			GSM-80	C	0.277	6.916		
GSG-72	B	4.961	48.062			GSM-92	C	0.597	8.955		
GSG-77	B	3.768	5.495			PS-158	D	3.512	35.119		
GSG-70	B	0.543	9.239			PS-154	D	0.507	11.283		

TABLE XV

Personals, Round I
Methods 1 and 3

		mg/m ³				mg/m ³		µg/m ³	
Filter				Filter					
No.	Co.#	#1 B.S.	#3 BaP	No.	Co.#	#1 B.S.	#3 BaP		
PS-155	D	1.620	18.694	PS-186	E	2.019	26.398		
PS-145	D	4.535	42.606	PS-193	E	0.158	14.646		
PS-141	D	0.251	7.776	PS-180	E	0.165	8.911		
PS-161	D	0.772	9.911	PS-220	E	1.115	7.187		
PS-157	D	1.030	11.070	PS-209	E	0.743	8.674		
PS-159	D	0.383	6.890	PS-205	E	0.684	11.218		
PS-136	D	0.369	0.861	PS-226	E	1.069	11.497		
PS-146	D	<0.137	0.550	PS-210	E	1.958	8.283		
PS-148	D	0.395	9.870	PS-215	E	1.268	13.225		
PS-151	D	0.390	7.808	PS-214	E	1.654	16.176		
PS-165	D	3.805	137.548	PS-204	E	1.336	7.219		
PS-164	D	0.878	0.220	PS-96	E	<0.129	6.468		
PS-138	D	3.028	51.903	PS-207	E	0.401	6.952		
PS-120	D	1.268	16.480	PS-168	E	0.262	10.105		
PS-122	D	0.381	7.496	PS-217	E	1.534	4.324		
PS-123	D	0.254	0.381	PS-102	E	1.176	13.072		
PS-119	D	1.551	10.979	PS-167	E	0.919	8.530		
PS-118	D	0.132	5.790	PS-208	E	0.541	11.892		
PS-131	D	4.837	37.908						
PS-124	D	3.296	37.569						
PS-111	D	2.508	26.339						
PS-134	D	0.257	0.309						
PS-129	D	3.886	17.419						
PS-114	D	1.754	24.285						
PS-109	D	1.307	11.503						
PS-104	D	2.691	19.223						
PS-105	D	1.969	30.200						
PS-110	D	0.815	8.830						
PS-183	E	0.676	0.743						
PS-192	E	<0.135	5.541						
PS-184	E	1.307	20.915						
PS-178	E	0.560	10.364						
PS-195	E	0.270	9.054						
PS-194	E	<0.135	5.541						
PS-187	E	0.802	6.818						
PS-173	E	0.830	1.314						
PS-174	E	<0.139	7.917						
PS-175	E	1.664	149.792						
PS-170	E	0.567	8.511						
PS-169	E	1.543	32.258						

TABLE XVI

Personals, Round II
Methods 1 and 3

Filter No.	Co.#	#1 B.S.	#3 BaP	Filter No.	Co.#	#1 B.S.	#3 BaP
P-300	A	0.661	1.004	P-431	B	0.872	1.265
P-301	A	1.228	0.859	P-434	B	4.533	92.068
P-304	A	2.624	8.978	P-438	B	0.413	6.887
P-305	A	4.429	1.343	P-439	B	0.870	0.377
P-311	A	<0.137	1.372	P-440	B	0.389	0.013
P-312	A	5.718	1.100	P-441	B	0.412	1.509
P-313	A	3.306	7.163	P-442	B	2.276	2.908
P-315	A	3.094	7.314	P-444	B	4.239	<0.012
P-321	A	2.766	0.567	P-445	B	<0.154	0.998
P-322	A	5.563	0.807	P-446	B	0.477	0.079
P-327	A	3.102	2.511	P-447	B	<0.159	0.351
P-329	A	1.654	9.323	P-452	B	3.962	12.520
P-333	A	1.791	1.185	P-454	B	2.649	0.993
P-334	A	0.299	0.284	P-462	B	7.987	19.968
P-341	A	6.316	4.737	P-463	B	13.249	124.606
P-343	A	0.525	0.538	P-465	B	5.041	0.829
P-344	A	6.618	20.221	P-467	B	8.333	5.128
P-345	A	2.747	1.511	P-1	C	0.563	6.892
P-346	A	0.304	1.824	P-2	C	0.642	10.911
P-347	A	3.388	4.472	P-6	C	2.310	8.016
P-349	A	3.314	0.274	P-8	C	0.611	3.056
P-350	A	0.140	0.335	P-11	C	0.620	0.496
P-353	A	4.309	5.646	P-12	C	4.212	28.261
P-354	A	2.148	0.604	P-15	C	0.784	1.765
P-355	A	0.138	0.898	P-17	C	1.438	16.078
P-357	A	2.160	0.508	P-18	C	0.675	3.104
P-360	A	3.208	0.042	P-19	C	0.907	4.145
P-363	A	4.301	0.768	P-21	C	2.399	5.682
P-365	A	0.270	0.324	P-22	C	1.496	12.968
P-366	A	2.482	0.657	P-24	C	1.311	12.713
P-400	B	2.144	18.989	P-25	C	1.558	41.558
P-404	B	0.591	2.246	P-31	C	1.754	1.350
P-405	B	0.288	0.791	P-32	C	<0.130	1.172
P-406	B	1.008	1.889	P-34	C	1.032	0.645
P-408	B	0.977	1.587	P-35	C	0.305	0.763
P-409	B	0.452	1.056	P-37	C	1.669	21.438
P-411	B	<0.141	0.987	P-38	C	0.728	1.310
P-413	B	3.347	24.268	P-39	C	0.770	2.953
P-418	B	<0.148	0.207	P-40	C	0.667	0.800
P-419	B	6.722	9.602	P-41	C	0.897	1.154
P-424	B	0.444	2.370	P-42	C	0.314	3.931
P-428	B	4.010	25.516	P-46	C	2.763	36.842
P-429	B	0.686	0.549	P-52	C	1.747	7.132
P-430	B	1.151	3.197	P-60	C	1.291	8.465

TABLE XVI

Personals, Round II
Methods 1 and 3

Filter No.	Co.#	#1 B.S.	#3 BaP	Filter No.	Co.#	#1 B.S.	#3 BaP
P-61	C	0.707	3.357	P-231	E	0.560	
P-69	C	0.577	2.742	P-234	E	2.125	1.700
P-74	C	0.290	0.725	P-239	E	0.516	3.742
P-105	D	1.505	4.925	P-243	E	0.280	1.401
P-108	D	4.412	1.738	P-245	E	0.139	0.473
P-112	D	3.755	1.252	P-247	E	0.255	1.250
P-114	D	7.612	27.165	P-248	E	0.441	5.294
P-117	D	2.552	0.606	P-250	E	0.264	0.581
P-118	D	5.196	15.209	P-253	E	4.831	2.093
P-120	D	7.407	3.567	P-255	E	0.817	0.441
P-123	D	13.171	42.927	P-257	E	0.294	1.912
P-124	D	1.573	9.174	P-258	E	0.735	1.765
P-126	D	5.556	32.828	P-260	E	0.588	5.441
P-129	D	1.990	5.721	P-262	E	2.649	0.364
P-132	D	1.385	8.816	P-263	E	0.139	0.723
P-136	D	3.947	26.579	P-265	E	0.504	0.319
P-137	D	0.375	1.061	P-268	E	0.420	0.672
P-148	D	<0.123	1.348	P-270	E	0.135	1.108
P-151	D	5.960	30.464	P-227	E	13.6	6.04
P-152	D	2.652	32.197				
P-153	D	3.399	17.778				
P-154	D	0.903	4.000				
P-156	D	0.131	0.262				
P-157	D	2.850	29.793				
P-158	D	0.382	3.312				
P-160	D	<0.132	0.861				
P-161	D	4.533	52.000				
P-164	D	12.306	160.622				
P-166	D	1.074	14.094				
P-167	D	0.648	4.404				
P-170	D	3.485	3.485				
P-171	D	0.533	0.613				
P-172	D	4.382	5.578				
P-200	E	<0.134	0.478				
P-201	E	1.979	2.902				
P-204	E	1.480	13.997				
P-206	E	0.255	0.535				
P-208	E	0.886	10.340				
P-209	E	0.684	0.725				
P-213	E	0.175	1.281				
P-215	E	0.501	0.363				
P-228	E	0.379	0.265				
P-230	E	0.504	4.538				

TABLE XVII

PERSONALS, ROUND I
METHOD 2 - GC-UV for 14 PNA's

$\mu\text{g}/\text{m}^3$

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBahA	BghIP	Ant
PS-1	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-6	A	4.4	2.7	N.D.	2.2	3.5	N.D.	2.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-12	A	0.6	2.8	N.D.	1.6	2.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-15	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-16	A	2.9	2.4	N.D.	6.2	8.3	N.D.	4.2	1.5	2.9	4.5	7.6	3.2	N.D.	N.D.
PS-18	A	N.D.	N.D.	N.D.	0.6	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-19	A	1.7	2.0	N.D.	0.9	0.9	N.D.	3.8	N.D.	3.5	3.9	18.1	N.D.	N.D.	N.D.
PS-20	A	N.D.	N.D.	N.D.	4.2	5.7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-26,28	A	N.D.	N.D.	N.D.	0.4	0.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-27	A	N.D.	2.1	N.D.	4.4	5.3	N.D.	1.9	1.5	3.7	3.7	5.3	N.D.	N.D.	N.D.
PS-29	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-30	A	N.D.	N.D.	N.D.	0.6	0.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-34	A	N.D.	N.D.	N.D.	3.1	3.6	N.D.	2.8	N.D.	2.2	2.8	5.1	N.D.	N.D.	N.D.
PS-37	A	N.D.	N.D.	N.D.	1.2	1.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-38	A	N.D.	N.D.	N.D.	2.9	1.4	N.D.	1.8	1.4	2.7	1.7	12.6	N.D.	3.6	N.D.
PS-40	A	N.D.	N.D.	N.D.	0.7	1.0	N.D.	1.4	N.D.	1.3	N.D.	N.D.	N.D.	N.D.	N.D.
PS-43	A	1.5	1.0	N.D.	4.1	2.5	N.D.	N.D.	N.D.	N.D.	N.D.	18.2	N.D.	N.D.	N.D.
PS-44	A	N.D.	N.D.	N.D.	1.2	1.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-48	A	0.9	1.0	N.D.	6.5	9.6	N.D.	6.5	N.D.	2.7	3.3	8.4	3.3	3.6	0.9
PS-51	A	N.D.	N.D.	N.D.	0.8	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-53	A	3.5	4.4	N.D.	9.7	13.2	N.D.	7.8	2.8	5.9	6.3	11.3	N.D.	4.9	N.D.
PS-54	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-57	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-64	A	N.D.	N.D.	N.D.	1.8	2.4	N.D.	2.5	N.D.	N.D.	1.5	N.D.	N.D.	N.D.	N.D.
PSG-3	A	N.D.	1.2	N.D.	4.9	5.7	N.D.	1.6	N.D.	N.D.	0.9	4.5	N.D.	N.D.	N.D.
PSG-7	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PSG-8	A	N.D.	0.7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PSM-1,5	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PSM-4	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PSM-6	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-38	B	N.D.	N.D.	N.D.	2.2	2.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-39	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-41	B	N.D.	N.D.	N.D.	0.4	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

B-45

TABLE XVII

PERSONALS, ROUND I
METHOD 2 - GC-UV for 14 PNA's

$\mu\text{g}/\text{m}^3$

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBaHA	BghIP	Ant
GSG-46	B	8.8	11.5	N.D.	11.4	19.2	N.D.	6.4	2.3	3.8	5.9	19.2	N.D.	4.1	0.7
GSG-47	B	N.D.	N.D.	N.D.	2.7	3.2	N.D.	1.5	N.D.	1.4	0.9	3.9	N.D.	N.D.	N.D.
GSG-48	B	0.6	1.0	N.D.	2.5	3.2	N.D.	1.3	1.0	2.5	0.7	4.8	N.D.	N.D.	N.D.
GSG-50	B	11.9	12.9	1.9	19.4	28.5	N.D.	11.9	2.6	8.7	8.7	24.6	N.D.	N.D.	3.0
GSG-51	B	1.2	2.0	N.D.	8.2	9.8	N.D.	5.5	N.D.	4.9	1.9	0.9	N.D.	N.D.	N.D.
GSG-54	B	N.D.	N.D.	N.D.	4.2	2.2	N.D.	4.6	N.D.	2.2	2.8	4.0	N.D.	N.D.	N.D.
GSG-58	B	1.1	0.9	N.D.	2.9	3.9	N.D.	1.7	N.D.	1.1	0.7	3.2	N.D.	N.D.	N.D.
GSG-59	B	3.7	5.3	N.D.	12.0	17.1	N.D.	6.9	3.0	6.3	7.6	15.7	N.D.	13.2	2.5
GSG-61	B	14.9	7.7	N.D.	14.9	21.6	N.D.	4.7	1.8	5.4	4.3	27.1	N.D.	9.1	4.3
GSG-62	B	1.0	0.7	N.D.	1.6	2.9	N.D.	1.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-73	B	N.D.	N.D.	N.D.	0.9	0.9	N.D.	2.9	N.D.	1.2	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-74	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-75	B	N.D.	N.D.	N.D.	0.9	0.7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-76	B	1.4	1.5	N.D.	6.7	8.6	N.D.	4.6	1.7	4.2	5.2	10.9	2.9	2.9	0.6
GSM-36	B	3.5	5.9	N.D.	6.8	9.1	N.D.	2.3	N.D.	2.3	3.0	8.9	N.D.	N.D.	N.D.
GSM-37	B	8.8	7.3	N.D.	11.7	16.6	N.D.	6.8	2.5	5.1	4.1	13.8	N.D.	6.5	1.2
GSM-38	B	19.9	21.3	1.6	7.5	14.2	N.D.	5.8	2.8	5.4	4.8	18.5	N.D.	7.5	2.8
GSM-40	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-43	B	N.D.	N.D.	N.D.	0.7	0.9	N.D.	0.6	N.D.	0.6	0.3	1.7	N.D.	N.D.	N.D.
GSM-44	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-46	B	N.D.	N.D.	N.D.	0.7	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-47	B	3.2	2.6	N.D.	3.7	4.6	N.D.	1.7	N.D.	N.D.	2.1	7.6	N.D.	N.D.	N.D.
GSM-51	B	N.D.	N.D.	N.D.	0.4	0.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-52	B	2.8	N.D.	N.D.	2.7	3.6	N.D.	1.5	N.D.	N.D.	1.9	6.7	N.D.	N.D.	N.D.
GSM-58	B	10.4	10.0	N.D.	12.0	17.6	N.D.	5.4	2.7	5.0	3.8	12.7	N.D.	5.1	1.6
GSM-61	B	16.1	10.1	3.6	18.8	25.5	N.D.	5.2	2.3	5.8	3.9	11.9	N.D.	N.D.	N.D.
GSM-62	B	8.0	9.8	2.0	5.2	5.0	N.D.	3.4	0.8	2.1	2.1	8.1	N.D.	N.D.	N.D.
GSG-66	C	N.D.	N.D.	N.D.	2.6	2.6	N.D.	3.7	N.D.	1.7	2.8	4.9	N.D.	3.6	N.D.
GSG-67	C	N.D.	6.3	N.D.	N.D.	N.D.	N.D.	12.2	N.D.	N.D.	12.5	35.7	N.D.	N.D.	N.D.
GSG-68	C	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-69	C	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-79	C	4.6	4.2	N.D.	6.0	7.4	N.D.	5.0	2.1	3.2	N.D.	N.D.	13.3	N.D.	N.D.
GSG-82	C	N.D.	0.3	N.D.	0.6	0.9	N.D.	1.7	N.D.	1.6	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-85	C	N.D.	N.D.	N.D.	1.5	1.8	N.D.	2.2	N.D.	2.0	2.0	2.9	N.D.	N.D.	N.D.

B-46

TABLE XVII

PERSONALS, ROUND I
METHOD 2 - GC-UV for 14 PNA's

µg/m³

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BeAn	BbF	BjF	BkF	BeP	BaP	DBaH	BghIP	Ant
GSG-86	C	4.5	5.2	N.D.	11.1	13.6	N.D.	11.3	4.6	5.3	4.3	10.9	N.D.	N.D.	4.1
GSG-87	C	N.D.	N.D.	N.D.	2.5	2.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-88	C	N.D.	N.D.	N.D.	0.7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-90	C	N.D.	N.D.	N.D.	1.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-91	C	N.D.	N.D.	N.D.	1.9	2.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-94	C	N.D.	N.D.	N.D.	1.4	2.4	N.D.	1.8	N.D.	1.6	1.6	N.D.	N.D.	N.D.	N.D.
GSG-98	C	N.D.	N.D.	N.D.	2.0	2.1	N.D.	1.0	N.D.	N.D.	N.D.	3.8	N.D.	N.D.	0.7
GSG-99	C	N.D.	0.9	N.D.	5.4	7.4	N.D.	3.0	1.0	2.8	2.8	5.4	N.D.	N.D.	N.D.
GSG-103	C	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSG-108	C	N.D.	N.D.	N.D.	1.6	1.9	N.D.	2.2	0.7	1.0	1.0	N.D.	N.D.	N.D.	N.D.
GSG-123	C	N.D.	N.D.	N.D.	5.3	3.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-72	C	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-74	C	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-79	C	N.D.	N.D.	N.D.	5.7	8.1	N.D.	3.7	N.D.	3.4	4.5	9.7	N.D.	N.D.	N.D.
GSM-81	C	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-84	C	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.7	N.D.	N.D.	1.6	N.D.	N.D.	N.D.	N.D.
GSM-85	C	0.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-86	C	N.D.	1.1	N.D.	9.3	9.6	N.D.	10.1	2.1	7.9	8.8	18.9	6.9	5.5	1.0
GSM-88	C	N.D.	N.D.	N.D.	0.8	0.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-89	C	N.D.	N.D.	N.D.	1.4	1.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-97	C	N.D.	1.1	N.D.	4.5	5.6	N.D.	3.1	0.7	1.9	2.4	3.5	N.D.	N.D.	N.D.
GSM-98	C	N.D.	N.D.	N.D.	0.8	1.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
GSM-100	C	N.D.	1.0	N.D.	1.6	3.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-98	D	N.D.	N.D.	N.D.	1.7	1.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-101	D	5.1	6.1	N.D.	7.5	12.1	N.D.	3.1	1.8	3.3	2.2	9.7	N.D.	N.D.	N.D.
PS-106	D	12.4	12.4	6.9	15.7	22.3	N.D.	13.1	3.0	11.3	10.9	24.9	N.D.	10.4	2.5
PS-113	D	14.4	12.5	4.1	21.0	32.8	N.D.	19.7	2.4	10.9	8.1	31.5	3.0	12.1	4.1
PS-115	D	N.D.	N.D.	N.D.	0.5	0.3	N.D.	N.D.	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	N.D.
PS-116	D	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-117	D	N.D.	N.D.	N.D.	3.0	2.3	N.D.	4.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-121	D	N.D.	N.D.	N.D.	5.5	8.1	N.D.	1.7	1.9	3.6	3.2	9.9	N.D.	N.D.	N.D.
PS-125	D	N.D.	N.D.	N.D.	1.0	1.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-126	D	0.7	1.0	N.D.	1.9	3.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-127	D	N.D.	N.D.	N.D.	2.0	2.1	N.D.	2.5	N.D.	1.1	2.2	2.1	N.D.	N.D.	N.D.

B-47

TABLE XVII

PERSONALS, ROUND I
METHOD 2 - GC-UV for 14 PNA's

$\mu\text{g}/\text{m}^3$

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBahA	BghiP	Ant
PS-128	D	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-130	D	29.4	25.4	N.D.	28.1	45.5	N.D.	12.2	N.D.	13.4	12.6	37.4	N.D.	11.6	5.8
PS-132	D	1.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	17.4	N.D.	N.D.
PS-133	D	N.D.	0.4	N.D.	3.7	5.5	N.D.	1.3	N.D.	1.1	1.6	4.0	N.D.	N.D.	N.D.
PS-137	D	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-139	D	0.9	N.D.	N.D.	2.3	2.4	N.D.	2.0	N.D.	1.9	2.4	N.D.	N.D.	N.D.	N.D.
PS-142	D	9.7	9.2	N.D.	15.0	21.9	N.D.	10.1	3.1	8.8	9.0	19.2	N.D.	N.D.	N.D.
PS-144	D	N.D.	N.D.	N.D.	1.3	N.D.	N.D.	N.D.	N.D.	N.D.	62.3	96.7	N.D.	N.D.	N.D.
PS-147	D	23.2	20.5	4.5	23.2	32.8	N.D.	13.1	2.9	12.0	15.0	35.5	N.D.	N.D.	N.D.
PS-149	D	0.5	0.9	N.D.	1.0	1.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-150	D	N.D.	0.8	N.D.	5.4	7.6	N.D.	3.1	N.D.	2.8	2.0	6.7	N.D.	2.9	0.9
PS-152	D	5.2	2.8	N.D.	7.3	10.8	N.D.	5.4	N.D.	4.9	4.5	11.7	N.D.	N.D.	N.D.
PS-153	D	2.1	3.6	N.D.	5.5	8.6	N.D.	30.3	1.7	5.4	5.1	8.7	N.D.	N.D.	N.D.
PS-156	D	N.D.	N.D.	N.D.	1.6	1.7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-160	D	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.7	2.0	2.5	N.D.	N.D.	N.D.	N.D.	N.D.
PS-162	D	3.3	2.4	N.D.	8.2	8.5	N.D.	2.9	N.D.	3.3	2.1	11.9	N.D.	N.D.	N.D.
PS-163	D	3.1	4.9	N.D.	17.6	26.4	N.D.	10.6	2.6	8.2	6.7	20.1	9.9	6.8	2.4
PS-89	E	4.5	5.2	N.D.	10.9	11.6	N.D.	7.8	2.8	7.2	5.9	15.4	N.D.	11.1	1.4
PS-92	E	N.D.	N.D.	N.D.	11.5	12.0	N.D.	9.0	N.D.	8.4	5.6	7.8	N.D.	N.D.	N.D.
PS-93	E	N.D.	N.D.	N.D.	0.4	0.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-95	E	N.D.	N.D.	N.D.	3.4	3.3	N.D.	1.3	N.D.	1.2	1.7	2.4	N.D.	N.D.	N.D.
PS-107	E	N.D.	N.D.	N.D.	2.2	0.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-108	E	N.D.	2.8	N.D.	32.1	38.8	N.D.	4.7	2.9	7.9	9.6	28.1	N.D.	10.6	3.7
PS-166	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-171	E	N.D.	N.D.	N.D.	5.1	4.9	N.D.	1.9	N.D.	N.D.	1.7	7.5	N.D.	N.D.	N.D.
PS-172	E	13.0	23.2	2.9	20.1	18.5	N.D.	5.3	3.9	8.0	7.6	27.8	N.D.	10.0	2.5
PS-176	E	N.D.	N.D.	N.D.	0.9	1.9	N.D.	N.D.	N.D.	N.D.	1.2	3.7	N.D.	N.D.	N.D.
PS-177	E	N.D.	N.D.	N.D.	1.1	1.2	N.D.	0.7	N.D.	N.D.	0.9	N.D.	N.D.	N.D.	N.D.
PS-179	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-181	E	N.D.	N.D.	N.D.	1.6	1.8	N.D.	N.D.	N.D.	1.5	0.9	2.2	N.D.	N.D.	N.D.
PS-182	E	N.D.	2.2	N.D.	6.3	4.9	N.D.	N.D.	N.D.	N.D.	3.6	5.0	N.D.	N.D.	N.D.
PS-185	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-188	E	N.D.	N.D.	N.D.	0.4	0.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-189	E	N.D.	N.D.	N.D.	3.0	2.0	N.D.	2.7	N.D.	2.5	2.5	3.7	N.D.	N.D.	N.D.

6-48

PERSONALS, ROUND I
METHOD 2 - GC-UV for 14 PNA's

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBahA	BghP	Ant
PS-191	E	2.3	2.3	1.6	5.1	6.6	N.D.	1.0	N.D.	2.8	1.8	5.3	N.D.	N.D.	N.D.
PS-197	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-198	E	N.D.	N.D.	N.D.	4.3	2.9	N.D.	4.9	N.D.	4.5	2.9	6.4	N.D.	N.D.	N.D.
PS-199	E	59.5	50.4	3.9	1.6	1.7	N.D.	1.7	N.D.	1.6	N.D.	N.D.	N.D.	N.D.	N.D.
PS-200	E	N.D.	N.D.	N.D.	2.1	2.0	N.D.	2.6	N.D.	N.D.	1.6	N.D.	N.D.	N.D.	N.D.
PS-206	E	N.D.	1.1	N.D.	4.8	3.8	N.D.	1.5	N.D.	N.D.	2.2	3.1	N.D.	N.D.	N.D.
PS-211	E	N.D.	N.D.	N.D.	4.1	2.2	N.D.	9.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-213	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	N.D.
PS-216	E	1.1	1.0	N.D.	1.8	1.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-219	E	N.D.	N.D.	N.D.	2.3	2.8	N.D.	2.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PS-221	E	0.8	0.7	N.D.	2.2	1.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SP-224	E	2.3	5.9	N.D.	12.6	15.0	N.D.	5.2	3.8	4.8	3.1	9.0	N.D.	N.D.	N.D.
PS-225	E	N.D.	N.D.	N.D.	6.9	6.8	N.D.	2.3	1.7	3.2	3.6	5.1	N.D.	4.5	0.8

B-49

TABLE XVIII

PERSONALS, ROUND II
METHOD 2 - GC-UV for 14 PNA's

 $\mu\text{g}/\text{m}^3$

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBaH	BghP	Ant
P-410	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-412	B	28.6	30.2	2.7	28.6	42.9	N.D.	19.1	4.4	13.0	14.1	31.8	N.D.	N.D.	N.D.
P-414	B	9.4	10.0	N.D.	18.6	27.2	N.D.	11.5	4.1	8.7	8.9	19.8	2.6	4.3	N.D.
P-415	B	N.D.	0.9	N.D.	5.1	6.2	N.D.	1.5	1.3	2.0	2.0	N.D.	N.D.	N.D.	N.D.
P-416	B	N.D.	1.1	4.7	0.7	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-417	B	N.D.	N.D.	N.D.	1.1	1.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5.3	1.5
P-421	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-422	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-423	B	N.D.	N.D.	N.D.	1.5	1.4	N.D.	2.2	1.6	2.0	1.5	N.D.	N.D.	N.D.	1.0
P-425	B	2.6	3.1	N.D.	10.4	13.7	N.D.	6.6	2.0	5.2	5.7	12.3	N.D.	7.3	2.0
P-426	B	N.D.	N.D.	N.D.	6.8	7.3	N.D.	4.7	1.7	4.3	2.8	N.D.	N.D.	9.0	1.7
P-427	B	10.9	12.1	3.0	11.0	14.9	N.D.	7.2	1.9	5.2	5.7	10.9	1.0	4.6	2.0
P-432	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-433	B	2.1	1.2	N.D.	9.8	12.6	N.D.	5.5	3.1	1.9	4.4	7.4	N.D.	N.D.	N.D.
P-435	B	0.7	1.0	4.5	1.9	0.9	N.D.	2.0	2.3	2.0	N.D.	N.D.	N.D.	6.0	1.6
P-436	B	N.D.	N.D.	N.D.	1.1	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-437	B	22.7	22.7	4.2	31.8	43.9	N.D.	19.7	3.8	13.9	16.6	37.8	N.D.	N.D.	N.D.
P-443	B	3.2	5.5	N.D.	8.1	10.4	N.D.	3.5	N.D.	3.2	4.4	9.4	N.D.	N.D.	N.D.
P-449	B	2.9	4.8	N.D.	16.0	22.4	N.D.	12.9	4.8	11.8	10.7	22.4	N.D.	12.3	2.2
P-450	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-451	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-453	B	0.6	3.4	2.6	8.3	11.7	N.D.	3.9	2.1	3.5	1.5	4.4	N.D.	6.3	1.4
P-457	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-459	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-464	B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-7	C	1.4	1.5	1.7	8.8	10.8	N.D.	8.3	2.2	5.7	5.1	7.2	N.D.	N.D.	N.D.
P-9	C	2.8	3.8	N.D.	12.2	17.8	N.D.	3.4	2.3	5.5	5.5	10.8	2.5	N.D.	N.D.
P-10	C	3.5	2.8	4.3	10.6	11.4	N.D.	0.5	N.D.	2.3	5.5	11.1	N.D.	4.3	0.9
P-13	C	5.5	5.7	1.3	8.6	11.7	N.D.	6.0	1.0	4.8	5.1	7.8	N.D.	4.3	0.5
P-14	C	N.D.	1.2	N.D.	5.0	5.2	N.D.	3.4	2.5	2.2	2.0	3.6	N.D.	N.D.	N.D.
P-16	C	10.0	8.3	N.D.	19.7	23.6	N.D.	12.3	3.0	7.5	8.3	17.1	N.D.	10.4	2.0
P-20	C	N.D.	N.D.	N.D.	2.9	2.5	N.D.	1.9	N.D.	2.7	1.8	1.6	N.D.	N.D.	N.D.
P-26	C	1.2	2.4	N.D.	0.7	0.8	N.D.	N.D.	N.D.	N.D.	1.5	2.5	N.D.	4.5	N.D.
P-27	C	N.D.	N.D.	N.D.	0.5	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

B-51

TABLE XVIII

PERSONALS, ROUND II
METHOD 2 - GC-UV for 14 PNA's

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBahA	BghiP	Ant
P-302	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-303	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-306	A	N.D.	N.D.	N.D.	0.3	0.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-308	A	5.2	6.2	N.D.	7.4	9.6	N.D.	6.6	N.D.	4.0	5.3	8.2	N.D.	N.D.	1.0
P-309	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-310	A	N.D.	1.0	N.D.	3.3	3.3	N.D.	5.6	2.8	N.D.	8.9	10.2	N.D.	N.D.	N.D.
P-314	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	N.D.
P-319	A	2.7	2.2	N.D.	3.3	5.1	N.D.	1.8	N.D.	1.8	N.D.	N.D.	N.D.	N.D.	N.D.
P-323	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	6.2	13.5	N.D.	N.D.	N.D.
P-324	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-325	A	3.4	3.3	N.D.	2.6	4.1	N.D.	1.0	N.D.	1.0	N.D.	N.D.	N.D.	N.D.	N.D.
P-326	A	N.D.	N.D.	N.D.	0.7	1.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-328	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-330	A	N.D.	N.D.	N.D.	0.1	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-331	A	N.D.	N.D.	N.D.	0.8	1.0	N.D.	N.D.	N.D.	N.D.	1.3	1.8	N.D.	N.D.	N.D.
P-332	A	7.0	6.8	N.D.	5.3	7.7	N.D.	4.7	1.8	4.3	4.3	7.2	N.D.	4.5	N.D.
P-335	A	N.D.	1.1	2.9	2.9	4.3	N.D.	1.7	1.2	N.D.	2.1	3.3	N.D.	N.D.	N.D.
P-336	A	N.D.	N.D.	N.D.	1.5	1.5	N.D.	2.1	N.D.	N.D.	1.3	1.8	N.D.	N.D.	N.D.
P-337	A	3.9	4.9	N.D.	18.7	23.9	N.D.	22.1	6.5	15.8	10.6	7.5	N.D.	N.D.	N.D.
P-338	A	1.4	2.5	N.D.	4.0	5.4	N.D.	4.0	1.2	2.7	2.7	3.7	N.D.	N.D.	N.D.
P-339	A	4.0	2.8	N.D.	4.0	6.0	N.D.	3.5	0.5	2.4	3.2	6.0	N.D.	3.4	0.5
P-340	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-342	A	3.4	2.4	N.D.	2.6	4.7	N.D.	3.4	N.D.	1.6	1.3	N.D.	N.D.	N.D.	N.D.
P-348	A	N.D.	0.5	N.D.	1.1	0.7	N.D.	1.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-351	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-352	A	1.4	1.8	N.D.	3.8	4.7	N.D.	N.D.	N.D.	N.D.	1.9	1.3	N.D.	N.D.	N.D.
P-356	A	N.D.	1.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-358	A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-362	A	2.3	1.4	N.D.	1.3	1.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-364	A	N.D.	N.D.	N.D.	2.2	2.5	N.D.	2.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-401	B	N.D.	N.D.	8.6	0.8	1.2	N.D.	N.D.	N.D.	1.4	1.7	N.D.	N.D.	N.D.	N.D.
P-402	B	N.D.	N.D.	N.D.	3.6	3.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-403	B	1.4	1.8	N.D.	5.1	4.8	N.D.	3.2	N.D.	4.2	3.8	4.1	N.D.	9.0	1.0
P-407	B	2.2	3.9	N.D.	9.0	10.4	N.D.	6.3	2.7	4.7	5.1	9.6	N.D.	5.9	1.0

8-50

TABLE XVIII

PERSONALS, ROUND II
METHOD 2 - GC-UV for 14 PNA's

µg/m³

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBahA	BghIP	Ant
P-28	C	N.D.	N.D.	N.D.	0.8	0.6	N.D.	2.7	0.5	1.3	N.D.	N.D.	N.D.	N.D.	N.D.
P-29	C	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-30	C	7.8	9.3	N.D.	16.4	14.0	N.D.	31.3	7.2	16.4	14.9	19.4	N.D.	19.4	1.8
P-33	C	1.8	1.1	N.D.	2.7	3.2	N.D.	2.4	2.7	N.D.	3.3	N.D.	4.7	N.D.	N.D.
P-36	C	1.2	0.9	N.D.	3.9	5.9	N.D.	2.5	2.0	2.5	3.1	17.0	N.D.	7.1	1.4
P-43	C	1.9	1.2	N.D.	5.2	5.8	N.D.	1.8	N.D.	2.3	N.D.	N.D.	N.D.	N.D.	N.D.
P-44	C	16.3	19.3	N.D.	26.3	35.1	N.D.	7.4	3.3	6.8	11.7	22.8	N.D.	5.6	1.6
P-45	C	4.2	2.9	N.D.	5.7	6.9	N.D.	4.8	N.D.	3.1	2.9	3.6	14.0	N.D.	N.D.
P-49	C	3.3	2.3	N.D.	7.8	5.5	N.D.	3.1	1.9	3.6	1.5	N.D.	N.D.	N.D.	N.D.
P-50	C	5.0	4.9	N.D.	8.5	10.9	N.D.	5.2	1.2	3.9	3.5	9.4	N.D.	5.6	N.D.
P-51	C	1.1	1.5	N.D.	2.1	5.0	N.D.	N.D.	N.D.	N.D.	1.7	N.D.	N.D.	1.4	N.D.
P-53	C	14.9	4.9	N.D.	17.9	23.9	N.D.	11.8	2.5	7.2	4.9	16.4	1.8	8.8	1.8
P-54	C	N.D.	N.D.	N.D.	1.9	1.5	N.D.	6.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-56	C	N.D.	1.0	1.5	1.6	7.4	N.D.	9.1	1.0	5.6	4.6	5.3	N.D.	N.D.	N.D.
P-57	C	29.9	28.6	2.2	23.4	31.3	N.D.	15.6	3.9	10.3	10.8	20.8	N.D.	4.9	0.4
P-58	C	N.D.	N.D.	N.D.	0.4	0.3	N.D.	N.D.	N.D.	1.1	N.D.	N.D.	N.D.	N.D.	N.D.
P-59	C	14.3	11.3	N.D.	15.7	20.0	N.D.	12.1	3.1	7.9	5.3	12.0	N.D.	4.9	0.9
P-62	C	5.0	5.1	1.4	18.4	22.7	N.D.	15.6	2.7	8.2	11.6	15.6	N.D.	10.3	1.0
P-63	C	3.1	3.3	N.D.	9.3	10.7	N.D.	3.4	N.D.	4.7	3.1	4.4	N.D.	N.D.	N.D.
P-65	C	1.3	1.3	3.5	9.2	8.7	N.D.	12.8	1.8	5.1	6.3	7.4	3.1	4.2	N.D.
P-100	D	25.9	25.9	6.5	22.0	33.7	N.D.	8.0	3.1	8.7	10.0	24.6	3.9	12.2	3.8
P-104	D	N.D.	N.D.	N.D.	3.3	3.4	N.D.	2.9	N.D.	1.8	1.8	2.6	N.D.	5.9	1.0
P-109	D	0.6	N.D.	N.D.	6.0	1.8	N.D.	2.3	N.D.	1.8	1.1	N.D.	N.D.	3.9	1.4
P-110	D	15.4	15.9	N.D.	23.0	32.8	N.D.	10.7	3.6	11.1	5.9	37.7	N.D.	N.D.	4.1
P-113	D	N.D.	N.D.	N.D.	2.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-115	D	14.6	13.4	13.5	22.0	29.9	N.D.	11.3	4.6	9.4	7.5	20.4	N.D.	15.7	3.8
P-119	D	10.0	11.1	6.2	15.6	20.7	N.D.	11.0	4.0	8.3	10.0	17.5	N.D.	N.D.	N.D.
P-125	D	7.5	10.0	N.D.	19.6	30.4	N.D.	9.8	6.1	8.9	13.4	41.1	N.D.	N.D.	N.D.
P-127	D	3.3	3.6	N.D.	9.0	13.8	N.D.	4.8	2.6	4.4	7.3	16.3	N.D.	9.2	2.1
P-128	D	1.7	2.4	2.2	10.4	15.3	N.D.	5.1	2.8	5.7	5.4	19.1	N.D.	N.D.	N.D.
P-130	D	2.6	1.7	N.D.	3.9	4.5	N.D.	3.0	2.9	3.0	3.5	N.D.	N.D.	N.D.	N.D.
P-131	D	9.0	8.9	2.0	15.9	23.8	N.D.	15.9	2.5	7.4	7.1	21.1	N.D.	18.5	3.8
P-133	D	N.D.	N.D.	3.9	1.0	0.4	N.D.	1.3	N.D.	N.D.	1.6	N.D.	N.D.	2.4	N.D.
P-138	D	N.D.	1.0	N.D.	1.4	1.5	N.D.	1.8	N.D.	N.D.	N.D.	N.D.	2.0	4.9	N.D.

B-52

TABLE XVIII

PERSONALS, ROUND II
METHOD 2 - GC-UV for 14 PNA's

µg/m³

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBaH	BghIP	Ant
P-139	D	N.D.	10.7	N.D.	14.7	25.4	N.D.	7.0	4.5	5.5	5.9	17.4	N.D.	11.5	3.6
P-141	D	N.D.	N.D.	N.D.	1.9	1.6	N.D.	2.1	1.2	0.7	2.1	N.D.	1.0	N.D.	N.D.
P-142	D	N.D.	N.D.	N.D.	2.4	2.9	N.D.	3.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-143	D	2.8	3.4	N.D.	8.8	12.6	N.D.	8.3	2.3	5.6	5.1	8.6	N.D.	5.8	0.8
P-144	D	N.D.	1.1	N.D.	6.1	8.6	N.D.	6.5	2.0	3.0	3.4	N.D.	N.D.	N.D.	N.D.
P-146	D	2.0	1.6	N.D.	2.0	2.1	N.D.	N.D.	N.D.	N.D.	2.7	3.5	N.D.	N.D.	N.D.
P-155	D	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-159	D	1.0	1.3	N.D.	1.4	2.1	N.D.	N.D.	N.D.	N.D.	1.3	3.9	N.D.	6.5	1.7
P-162	D	4.2	2.8	N.D.	2.9	4.0	N.D.	N.D.	N.D.	N.D.	2.8	5.4	N.D.	N.D.	N.D.
P-163	D	1.7	1.3	N.D.	8.2	12.2	N.D.	1.2	N.D.	2.3	4.9	7.8	N.D.	N.D.	N.D.
P-165	D	N.D.	0.4	N.D.	0.9	0.8	N.D.	1.0	0.5	1.3	N.D.	N.D.	N.D.	N.D.	N.D.
P-168	D	1.1	1.3	N.D.	4.4	4.0	N.D.	2.4	0.8	2.1	2.1	3.0	N.D.	N.D.	N.D.
P-169	D	61.0	49.4	10.1	46.8	64.9	N.D.	24.7	6.9	18.2	10.8	35.1	N.D.	20.8	8.7
P-173	D	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-174	D	N.D.	N.D.	N.D.	1.5	1.1	N.D.	3.6	N.D.	N.D.	2.1	N.D.	N.D.	7.4	N.D.
P-175	D	0.7	0.5	N.D.	4.3	5.9	N.D.	2.9	1.3	2.6	2.1	2.6	N.D.	N.D.	N.D.
P-202	E	5.1	6.4	N.D.	4.9	6.2	N.D.	3.8	N.D.	3.4	4.6	9.8	N.D.	N.D.	N.D.
P-211	E	3.0	5.2	N.D.	6.2	9.7	N.D.	2.7	1.0	3.7	5.9	14.3	N.D.	5.2	1.0
P-212	E	N.D.	N.D.	N.D.	0.4	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-214	E	N.D.	N.D.	N.D.	6.4	5.0	N.D.	2.7	1.0	3.6	3.2	4.6	N.D.	N.D.	N.D.
P-216	E	45.9	35.2	6.4	24.5	33.7	N.D.	5.7	3.5	7.8	6.3	16.8	N.D.	7.2	1.4
P-217	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	9.4	12.2	N.D.	N.D.	N.D.
P-218	E	N.D.	0.4	N.D.	0.8	0.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-219	E	1.6	0.6	N.D.	2.4	2.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-220	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-221	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-223	E	N.D.	N.D.	N.D.	2.2	1.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-224	E	N.D.	N.D.	N.D.	0.7	0.6	N.D.	1.3	N.D.	N.D.	0.9	2.3	N.D.	N.D.	N.D.
P-225	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-226	E	N.D.	3.6	N.D.	7.8	8.9	N.D.	4.5	N.D.	3.8	4.2	6.5	N.D.	N.D.	N.D.
P-232	E	2.6	2.6	N.D.	4.7	3.9	N.D.	3.5	0.8	3.1	2.8	4.1	N.D.	N.D.	N.D.
P-233	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-236	E	N.D.	1.0	N.D.	2.1	1.8	N.D.	1.3	N.D.	1.1	1.5	2.2	N.D.	2.5	0.4
P-237	E	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

B-53

PERSONALS, ROUND II
METHOD 2 - GC-UV for 14 PNA's

Filter No.	Co.#	Flu	Pyr	BcA	Chr	BaA	BaAn	BbF	BjF	BkF	BeP	BaP	DBahA	BghiP	Ant
P-238	E	N.D.	0.4	N.D.	3.2	2.2	N.D.	2.8	N.D.	2.5	1.7	2.4	N.D.	N.D.	N.D.
P-240	E	3.5	0.9	N.D.	8.8	7.4	N.D.	5.1	N.D.	4.7	4.7	8.9	N.D.	N.D.	N.D.
P-244	E	N.D.	N.D.	46.8	2.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-251	E	1.0	1.7	N.D.	3.0	7.1	N.D.	N.D.	N.D.	N.D.	N.D.	3.6	3.2	N.D.	N.D.
P-252	E	66.3	48.9	4.7	19.2	24.4	N.D.	10.5	1.9	7.5	7.2	15.7	N.D.	6.6	2.3
P-254	E	N.D.	N.D.	N.D.	1.2	1.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-259	E	N.D.	N.D.	N.D.	3.0	2.6	N.D.	1.9	N.D.	0.8	1.8	2.6	N.D.	N.D.	N.D.
P-264	E	N.D.	0.8	N.D.	2.1	1.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-266	E	N.D.	0.7	N.D.	1.0	0.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P-269	E	4.4	5.2	N.D.	6.9	6.9	N.D.	5.7	2.9	5.3	3.4	6.7	N.D.	3.6	0.6

B-54

TABLE XIX

Charcoal Tubes, Round I
Method 7, Solvent Vapors

			$\mu\text{g}/\text{m}^3$			
C.T. No.	Sec. No.	Co.#	Benzene	Toluene	Xylene	Napthalene
4068	A	B-6	2092.0	190.2	92.0	1245.4
	B		41.1	14.1	3.7	0.0
4069	A	B-5	1817.0	261.4	143.8	712.4
	B		477.1	13.7	3.3	0.0
4007	A	C-6	486.9	130.9	78.5	146.6
	B		31.9	11.5	1.0	0.0
4008	A	C-5	560.2	109.9	42.9	146.6
	B		50.8	15.7	5.2	0.0
4009	A	C-4	317.9	97.4	66.7	76.9
	B		564.1	20.0	4.1	0.0
4101	A	C-3	882.4	164.7	64.7	311.8
	B		70.6	21.8	30.0	0.0
4102	A	C-2	981.0	234.2	88.6	405.1
	B		107.6	25.9	41.1	0.0
4103	A	C-1	1390.8	304.6	137.9	643.7
	B		86.2	11.5	2.3	0.0
4104	A	C-9	1093.0	271.3	147.3	217.1
	B		85.3	14.0	1.6	0.0
4105	A	C-8	1357.1	267.9	125.0	Trace
	B		6.2	13.4	0.0	N.D.
4106	A	C-7	979.4	283.5	211.3	5.7
	B		2.4	0.0	0.0	0.0
4107	A	C-12	890.1	261.8	125.7	356.0
	B		17.3	12.6	2.1	0.0
4108	A	C-10	337.1	84.3	44.4	78.7
	B		29.8	10.7	3.4	0.0
4109	A	C-11	863.9	207.1	88.8	242.6
	B		67.5	4.7	0.0	0.0
3802	A	D-2	920.5	331.8	172.9	266.4
	B		13.1	10.7	1.9	N.D.
3803	A	D-3	221.6	73.9	39.8	N.D.
	B		3.8	N.D.	N.D.	N.D.
3804	A	D-9	757.3	786.4	996.8	851.1
	B		692.6	313.9	190.9	113.3
3805	A	D-8	1205.2	489.1	288.2	812.2
	B		358.1	87.3	40.6	93.0
3806	A	D-7	4067.8	926.6	830.5	457.6
	B		9.0	20.9	N.D.	N.D.
3807	A	D-12	1775.5	806.1	341.8	1306.1
	B		102.0	19.4	13.3	N.D.
3808	A	D-11	1174.9	431.7	251.4	519.1
	B		16.9	10.9	3.3	N.D.
3809	A	D-10	313.5	79.0	46.6	82.9
	B		19.4	2.1	0.3	N.D.

Pages B-55 & B-56 are blank

TABLE XIX

Charcoal Tubes, Round I
Method 7, Solvent Vapors

µg/m³

C.T. No.	Sec. No.	Co.#	Benzene	Toluene	Xylene	Napthalene
4051	A	A-1	1250.0	272.0	147.0	345.6
	B		279.4	42.6	8.1	9.6
4052	A	A-3	454.0	114.3	50.8	152.4
	B		23.5	10.5	0.6	0.0
4053	A	A-2	193.8	55.0	24.4	44.4
	B		15.6	13.1	1.3	0.0
4054	A	A-5	621.1	155.3	80.7	229.8
	B		4.3	10.6	1.9	0.0
4055	A	A-4	335.3	63.6	37.6	75.1
	B		63.6	5.8	1.2	0.0
4056	A	A-6	334.4	97.0	66.9	100.3
	B		23.4	6.4	0.7	0.0
4058	A	A-7	515.5	130.4	74.5	87.0
	B		43.5	2.5	0.0	0.0
4059	A	A-9	258.9	80.4	38.8	25.0
	B		58.0	9.8	0.9	0.0
4060	A	A-8	430.5	149.0	7.0	4.6
	B		0.0	0.0	0.0	0.0
4061	A	A-11	75.9	32.9	6.3	17.7
	B		4.4	15.8	5.1	0.0
4062	A	A-12	135.8	34.7	16.8	37.6
	B		10.4	6.4	1.2	0.0
4063	A	A-10	326.2	26.7	1.1	0.0
	B		0.0	0.0	0.0	0.0
4001	A	B-9	767.6	183.8	102.7	189.2
	B		54.6	7.6	0.0	0.0
4002	A	B-8	408.9	59.1	37.9	88.7
	B		64.0	0.0	1.5	0.0
4003	A	B-7	933.0	240.2	134.1	134.1
	B		61.5	0.0	0.0	0.0
4004	A	B-10	922.6	232.1	142.9	160.7
	B		77.4	14.3	3.0	0.0
4005	A	B-12	2109.2	504.2	327.7	1100.8
	B		176.5	20.2	4.2	19.3
4006	A	B-11	1955.2	470.1	283.6	985.1
	B		283.6	40.3	11.9	33.6
4064	A	B-1	1021.7	141.3	84.8	250.0
	B		652.2	0.0	0.0	0.0
4065	A	B-3	743.8	200.0	81.3	112.5
	B		3.5	8.8	0.0	0.0
4066	A	B-2	415.3	109.3	76.5	120.2
	B		82.0	17.5	6.0	0.0
4067	A	B-4	2103.1	474.2	299.0	247.4
	B		134.0	16.5	2.1	0.0

TABLE XIX

Charcoal Tubes, Round I
Method 7, Solvent Vapors

 $\mu\text{g}/\text{m}^3$

C.T. No.	Sec. No.	Co.#	Benzene	Toluene	Xylene	Napthalene
4010	A	D-1	439.0	122.0	69.7	80.1
	B		20.6	8.0	2.1	N.D.
4078	A	D-5	1567.0	871.1	494.8	948.5
	B		201.0	12.4	2.6	N.D.
4079	A	D-6	785.0	177.6	79.4	215.0
	B		60.7	9.3	7.0	N.D.
4080	A	D-4	934.8	239.1	108.7	157.6
	B		65.2	19.6	4.9	N.D.
4018	A	E-6	1132.6	436.5	215.5	569.1
	B		66.3	13.3	2.2	11.6
4019	A	E-4	541.9	162.6	64.0	44.8
	B		5.4	22.7	N.D.	N.D.
4020	A	E-9	751.3	254.0	169.3	301.6
	B		68.8	3.7	N.D.	N.D.
4021	A	E-8	458.1	223.5	178.8	290.5
	B		38.5	7.3	3.4	N.D.
4022	A	E-7	847.0	393.4	245.9	322.4
	B		5.5	9.8	1.1	N.D.
4110	A	E-3	1419.8	364.2	148.1	703.7
	B		104.9	37.0	N.D.	N.D.
4111	A	E-2	574.2	219.4	116.1	264.5
	B		13.5	12.9	N.D.	N.D.
4112	A	E-1	674.8	219.5	146.3	146.3
	B		146.3	13.0	9.8	N.D.
4113	A	E-5	1289.6	398.9	213.1	775.9
	B		30.1	6.0	0.5	N.D.
4301	A	E-11	987.7	277.8	166.7	345.7
	B		98.8	11.1	2.5	N.D.
4302	A	E-10	1065.2	380.4	222.8	429.3
	B		380.4	12.0	0.5	N.D.
4303	A	E-12	777.1	277.1	168.7	385.5
	B		23.5	11.4	4.8	N.D.

TABLE XX

Charcoal Tubes, Round II
Method 7, Solvent Vapors

C.T. No.	Sec. No.	Co.#	$\mu\text{g}/\text{m}^3$			
			Benzene	Toluene	Xylene	Napthalene
3654	A	A-22	888.9	N.D.	N.D.	120.4
	B		159.2	N.D.	N.D.	N.D.
3252	A	A-25	1013.3	251.3	136.0	120.7
	B		158.0	1.3	1.3	N.D.
3258	A	A-32	734.3	53.1	70.6	13.4
	B		258.7	N.D.	N.D.	N.D.
3256	A	A-27	840.2	98.2	74.0	69.8
	B		364.5	N.D.	N.D.	N.D.
3254	A	A-28	673.2	59.0	51.2	42.9
	B		175.1	N.D.	1.5	N.D.
3259	A	A-31	545.4	N.D.	N.D.	89.3
	B		754.0	N.D.	N.D.	N.D.
3656	A	A-23	3553.5	N.D.	N.D.	6.0
	B		283.2	N.D.	N.D.	N.D.
3253	A	A-26	605.4	93.0	67.0	55.7
	B		151.3	22.7	N.D.	N.D.
3655	A	A-21	1480.0	N.D.	N.D.	190.8
	B		180.0	N.D.	N.D.	N.D.
3251	A	A-24	4297.9	142.0	87.2	79.2
	B		33936.2	48.9	0.5	N.D.
3255	A	A-29	16651.4	66.5	55.5	48.2
	B		43027.5	115.1	16.5	N.D.
3257	A	A-30	724.3	57.8	68.1	39.5
	B		124.9	N.D.	3.8	N.D.
3261	A	B-23	1131.4	N.D.	N.D.	407.0
	B		1389.7	N.D.	N.D.	N.D.
3401	A	B-26	724.4	N.D.	N.D.	372.4
	B		122.2	N.D.	N.D.	N.D.
3405	A	B-29	5701.8	322.4	188.2	217.5
	B		139.5	4.4	0.4	N.D.
3408	A	B-32	2650.0	N.D.	N.D.	855.6
	B		131.7	N.D.	N.D.	N.D.
3262	A	B-22	2326.8	N.D.	N.D.	551.2
	B		119.5	N.D.	N.D.	N.D.
3402	A	B-25	346.1	N.D.	N.D.	18.0
	B		325.2	N.D.	N.D.	N.D.
3404	A	B-28	778.3	300.9	158.5	495.3
	B		200.5	118.9	N.D.	N.D.
3409	A	B-31	1120.5	N.D.	N.D.	187.3
	B		186.1	N.D.	N.D.	N.D.
3263	A	B-21	1984.2	N.D.	N.D.	455.9
	B		1685.0	N.D.	N.D.	N.D.
3403	A	B-24	2552.8	N.D.	N.D.	794.0
	B		341.7	N.D.	N.D.	N.D.

TABLE XX

Charcoal Tubes, Round II
Method 7, Solvent Vapors

C.T. No.	Sec. No.	Co.#	$\mu\text{g}/\text{m}^3$			
			Benzene	Toluene	Xylene	Napthalene
3406	A	B-27	10837.4	447.8	295.6	242.4
	B		174.9	1.0	2.5	N.D.
3407	A	B-30	1666.7	N.D.	N.D.	420.1
	B		539.6	N.D.	N.D.	N.D.
3705	A	C-26	42315.7	332.6	155.3	478.4
	B		40052.6	125.8	5.8	N.D.
3707	A	C-24	85272.7	386.4	158.2	473.6
	B		77454.5	232.7	12.7	N.D.
3703	A	C-22	42055.6	325.5	136.1	583.3
	B		32222.2	82.8	N.D.	N.D.
3704	A	C-21	42275.1	539.7	244.4	957.7
	B		48306.9	173.0	32.8	N.D.
3706	A	C-25	50500.0	346.0	144.0	690.0
	B		37950.0	87.5	3.5	N.D.
3702	A	C-23	33315.8	295.3	135.3	547.4
	B		30421.0	63.7	4.2	N.D.
3721	A	C-30	7042.8	370.0	131.4	230.0
	B		N.D.	11.4	N.D.	N.D.
3720	A	C-31	6435.7	202.8	89.3	193.6
	B		10571.4	33.6	N.D.	N.D.
3722	A	C-32	7357.1	186.4	94.3	132.8
	B		7714.3	8.6	0.7	N.D.
3716	A	C-29	45684.2	531.6	278.4	1094.7
	B		42368.4	155.8	5.8	N.D.
3715	A	C-27	50909.0	180.9	86.8	67.3
	B		34090.9	130.9	6.8	N.D.
3714	A	C-28	4378.9	180.5	88.4	168.9
	B		8436.8	10.0	N.D.	N.D.
3154	A	D-25	2780.8	808.2	493.2	1000.0
	B		N.D.	40.6	6.4	N.D.
3159	A	D-28	3021.8	1240.4	1005.5	1076.5
	B		301.1	138.2	25.1	N.D.
3157	A	D-24	2204.2	439.4	229.6	303.5
	B		N.D.	38.7	2.8	N.D.
3155	A	D-26	1319.6	685.6	459.8	419.6
	B		N.D.	45.4	5.7	N.D.
3158	A	D-29	2625.0	1005.4	619.6	826.1
	B		356.0	92.4	5.4	N.D.
3184	A	D-32	897.8	277.4	116.7	120.4
	B		4505.4	46.2	3.2	N.D.
3152	A	D-22	700.0	424.7	354.7	626.3
	B		N.D.	38.9	2.1	N.D.
3151	A	D-23	403.0	143.5	73.5	77.8
	B		N.D.	N.D.	N.D.	N.D.

TABLE XX

Charcoal Tubes, Round II
Method 7, Solvent Vapors

C.T. No.	Sec. No.	Co.#	$\mu\text{g}/\text{m}^3$			
			Benzene	Toluene	Xylene	Napthalene
3352	A	E-22	2475.8	223.4	138.7	579.0
	B		675.0	N.D.	N.D.	N.D.
3303	A	E-25	1025.2	37.4	22.7	30.3
	B		621.2	6.6	N.D.	N.D.
3168	A	E-28	3136.4	356.8	196.0	385.8
	B		1102.3	15.9	0.6	N.D.
3652	A	E-31	2033.5	184.4	126.8	226.2
	B		770.9	N.D.	6.1	N.D.
3304	A	E-29	1333.3	53.2	44.1	47.8
	B		6881.7	7.0	2.1	N.D.
3353	A	E-23	2060.2	103.0	40.6	318.0
	B		1097.7	2.2	N.D.	N.D.
3301	A	E-26	3319.8	273.6	129.4	68.0
	B		731.0	N.D.	2.5	N.D.
3653	A	E-32	3428.6	154.8	111.4	175.4
	B		685.7	N.D.	N.D.	N.D.
3351	A	E-21	1754.3	125.7	73.1	100.6
	B		1142.8	1.7	N.D.	N.D.
3302	A	E-24	1645.9	167.5	85.2	115.8
	B		617.2	N.D.	N.D.	N.D.
3305	A	E-27	2166.7	164.6	96.5	121.2
	B		681.8	5.0	2.0	N.D.
3651	A	E-30	1990.0	183.6	134.8	250.2
	B		701.5	5.0	0.5	N.D.

APPENDIX C

CONTENTS

1. Memorandum dated October 30, 1972; from Experimental Statistics Section, DLCD to Physical and Chemical Analysis Branch; subject: "Correlations between certain pair-wise combinations of four chemical analytical methods used on four sampling methods for the Coal Tar Pitch Study."
2. Memorandum dated February 14, 1973; from Statistical Services Section, DLCD to Physical and Chemical Analysis Branch; subject: "Determination of sampling and analytical errors in data from Coal Tar Pitch Volatiles Study."
3. Memorandum dated March 29, 1973; from Statistical Services Section, DLCD to Physical and Chemical Analysis Branch; subject: "Correlations between trace metal concentrations and coal tar pitch volatile concentrations determined by several chemical analytical methods."
4. Memorandum dated April 12, 1973; from Statistical Services Section, DLCD to Physical and Chemical Analysis Branch; subject: "Report on statistical analysis of coal-tar pitch volatile data from Union Carbide contract."

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
HEALTH SERVICES AND MENTAL HEALTH ADMINISTRATION
National Institute For Occupational Safety And Health

TO : John V. Crable
Chief, Physical and Chemical Analysis Branch, DLCD
Kathleen A. Schulte
Chemist, Physical and Chemical Analysis Branch, DLCD

DATE: October 30, 1972

FROM : Richard W. Hornung, Mathematical Statistician
Experimental Statistics Section, DLCD
Through: Kenneth A. Busch *KAB*
Chief, Experimental Statistics Section, DLCD

SUBJECT: Correlations between certain pair-wise combinations of four chemical analytical methods used on four sampling methods for the Coal Tar Pitch Study.

In response to your request for statistical services, a series of correlations on the Coal Tar Pitch data have been done. Using a program written for the Wang 720 computer, the correlation coefficient, 95% confidence limits on the coefficient, the covariance, and a t-test for zero correlation all were computed. In addition the means and the variances were calculated for the sets of data being compared.

A correlation coefficient of zero implies that there is no relationship between the two sets of data. The probability given in the print-out is the statistical probability that the computed correlation coefficient or a larger one would occur by chance, even if the true correlation had a value of zero. Therefore, very small probabilities indicate that there is very little likelihood that the true correlation has a zero value. Any such probability less than .05 is generally considered statistically significant. Correlation coefficients range from -1 to 1, with negative values indicating that one of the two sets of data increases as the other decreases, and positive values indicating that both sets move in the same direction.

The statistical information listed above for 18 pair-wise combinations of the analytical methods used with four sampling methods has been enclosed. Each combination is divided into Round 1 and Round 2, depending upon the two times of the year that the samples were taken. The results have been summarized in Table 1 of this memorandum.

Interpretation of Results.

As requested, correlations of 18 different pair-wise comparisons of four analytical methods were computed. These were taken from four different sampling methods, Hi-Vols, Personals, Horizontal Elutriator and Gross (S & G). Upon inspection of the enclosed print-outs, it appears that there are certain significant trends. For simplicity, the results will be broken down by degree of correlation i.e., high (greater than .8), moderate (between .8 and .6), and low (less than .6).

As was expected, the highest correlation occurred between the totals for

Preceding page blank

the 14 PNA's and the totals for the 6 TPC's. The correlations were generally greater than .9 for all four sampling methods in each of the two rounds, the range being .869 to .993. This indicates that the 6 TPC total is very nearly proportional to the 14 PNA total, and is a good measure of the degree of concentration of these types of chemical compounds. Because these two methods were so highly correlated, further analysis was done on them to determine the regression coefficients (slopes) of the lines through the data points. There were 8 different lines, one for each of the two rounds in all four sampling methods. The slopes varied to some degree among the sampling methods, the values ranging from .343 to .683. However, the slopes seemed to correspond very closely to the ratio of the two means in each case. This indicates that the regression line passes through, or very close to the origin. Therefore the slopes or the ratios of the means represent good estimates of the average proportion of the PNA total that is made up by the 6 TPC's

Also showing high correlation was B.S. (Benzene Soluble) versus BaP concentrations from Analytical Method 3. This was true, however, only with the High Volume and Horizontal Elutriator sampling methods. These correlations ranged from .713 to .970, the average being approximately .87. The correlations for this combination using Gross (S & G) and Personal sampling methods were considerably lower. In fact, in the case of the Gross (S & G) sampling method in Round 2, the t-test indicated that the correlation was not significantly different from zero. Noting this result, it would appear that the B.S. and BaP analytical methods are not nearly as strongly related over the whole range of sampling methods as is the 14 PNA's and the 6 TPC's. This may have considerable bearing on any decision as to whether or not to eliminate one of the two techniques.

The only other highly correlated combination was BaP (Method 3) versus BaP (Method 4). However, BaP (Method 2) was not highly correlated with BaP from either of Methods 3 or 4.

The combinations that showed moderate correlation (.6 to .8) were B.S. vs. 14 PNA total, duplicate PNA's from Methods 2 & 4, B.S. vs. 6 TPC total (all from the High Volume sampling method), and B.S. vs. 6 TPC total from the Gross (S & G) sampling method.

All other combinations showed a low correlation (less than .6), and in a few instances the t-test indicated no significant difference from zero. For this reason the data suggests that these combinations should not be considered as substitutes for each other.

In summary, the only combination that is evidently equivalent is the 14 PNA total versus 6 TPC total. It is rather a subjective decision as to

whether to treat B.S. versus BaP from Method 3 in the same manner, since the correlations varied greatly over the four sampling methods. I would recommend that, if possible, further data be gathered on these two methods. In view of the fact that BaP from Method 4 is also highly correlated with BaP from Method 3, there is a strong possibility that Analytical Method 3 may be eliminated. There seems to be no justification for similar action in any of the other cases.

If there are any further questions, please don't hesitate to call me at Extension 3140.

Richard W. Hornung
Richard W. Hornung

Enclosures

CC: Dr. Edward J. Fairchild, II
Mr. John M. Bryant
Mr. Jeremiah R. Lynch
Mr. Jerome Flesch

Table 1

<u>Combinations</u>	<u>Hi-Vols</u>		<u>r</u>		<u>Student's t- Test for r=0 Probability</u>	
	<u>n</u>		<u>r</u>			
	Rd.1	Rd.2	Rd.1	Rd.2	Rd.1	Rd.2
B.S. vs. 14 PNA's	60	60	.581	.784	.0000	.0000
B.S. vs. 6 TPC's	60	60	.608	.776	.0000	.0000
B.S. vs. BaP (Method 3)	60	60	.713	.970	.0000	.0000
BaP (Method 2) vs. BaP (Method 3)	60	60	.536	.558	.0000	.0000
BaP (Method 2) vs. BaP (Method 4)	60	60	.582	.479	.0000	.0001
BaP (Method 3) vs. BaP (Method 4)	60	60	.776	.973	.0000	.0000
Duplicate PNA's from Methods 2&4	60	60	.601	.704	.0000	.0000
14 PNA's vs. 6 TPC's	60	60	.956	.939	.0000	.0000

<u>Personals</u>					
14 PNA's vs. 6 TPC's	122	120	.931	.959	.0000 .0000
B.S. vs. BaP (Method 3)	144	148	.564	.635	.0000 .0000

<u>Horizontal Elutriator</u>					
14 PNA's vs. 6 TPC's	20	18	.993	.869	.0000 .0000
B.S. vs. BaP (Method 3)	10	9	.934	.884	.0001 .0016
B.S. vs. 14 PNA's	10	8	.726	.359*	.0175 .3832
B.S. vs. 6 TPC's	10	8	.712	.437*	.0208 .2792

<u>Gross (S & G)</u>					
14 PNA's vs. 6 TPC's	20	18	.988	.944	.0000 .0000
B.S. vs BaP (Method 3)	10	9	.818	.489*	.0038 .1815
B.S. vs. 14 PNA's	10	8	.383*	.791	.2746 .0193
B.S. vs. 6 TPC's	10	8	.469*	.781	.1720 .0221

* No significant difference from zero.

Preceding page blank

Hi-Vols

B.S. vs. BaP from Method 3

Round 1

	<u>B.S.</u>	<u>n</u> 60	<u>BaP</u>
Mean	1.556783333		15.510383333
Variance	1.621053291		212.040350174

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.713098241	.560662471	.818785081

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
7.746501745	.000000000	13.220785779

Round 2

	<u>n</u> 60	
Mean	3.379100000	38.077383333
Variance	26.100926803	4592.326402880

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.970431326	.950793749	.982302896

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
30.618381526	.000000000	335.976689081

Hi-Vols

14 PNA's vs. 6 TPC's from Method 2

Round 1

	<u>14 PNA's</u>	<u>N</u> 60	<u>6 TPC's</u>
Mean	137.960900000		59.680566666
Variance	58652.405175500		7562.154751030

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.955628404	.926526280	.973362878

<u>Test for r=0</u> <u>t-value</u>	<u>Test for r=0</u> <u>Probability</u>	<u>Covariance</u>
24.706279729	.000000000	20125.873706700

Round 2

	<u>N</u> 60	
Mean	188.070416666	73.944166666
Variance	33572.369492300	5062.468857450

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.939164180	.899816803	.963355785

<u>Test for r=0</u> <u>t-value</u>	<u>Test for r=0</u> <u>Probability</u>	<u>Covariance</u>
20.824210472	.000000000	12243.728751600

Hi-Vols

BaP (Method 3) vs. BaP (Method 4)

Round 1

	<u>Method 3</u>	<u>N</u> 60	<u>Method 4</u>
Mean	15.543716666		28.009433333
Variance	213.567736615		709.190874589

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.776220996	.650480700	.860547972

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
9.376509880	.000000000	302.088907161

Round 2

	<u>N</u> 60	
Mean	38.078383333	58.849833333
Variance	4592.311689880	14403.138348700

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.973137848	.955256950	.983931634

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
32.191354264	.000000000	7914.411160080

Hi-Vols

B.S. vs. 14 PNA's from Method 2

Round 1

	<u>14 PNA's</u>	<u>N</u> 60	<u>B.S.</u>
Mean	137.960900000		1.556833333
Variance	58652.405176700		1.619466073

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.580779467	.383347080	.727454236

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
5.433353168	.000001146	178.994667983

Round 2

		<u>N</u> 60
Mean	188.072083333	3.373600000
Variance	33573.360216900	26.096702244

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.783899727	.661652186	.865552140

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
9.615273303	.000000000	733.754425508

Hi-Vols

B.S. vs. 6 TPC's from Method 2

Round 1

	<u>6 TPC's</u>	<u>N</u> 60	<u>B.S.</u>
Mean	59.680566666		1.557666666
Variance	7562.154751030		1.618275819

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.607695234	.418274093	.746463241

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
5.827552206	.000000261	67.225630327

Round 2

	<u>N</u> 60	
Mean	73.944166666	3.378600000
Variance	5062.468857450	26.096702244

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.776262048	.650540281	.860574769

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
9.377757629	.000000000	282.151492355

Hi-Vols

Duplicate PNA's from Methods 2&4

Round 1

	<u>Method 2</u>	<u>n</u> 60	<u>Method 4</u>
Mean	114.309166666		182.109416666
Variance	43971.957238300		38051.946368300

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.600665509	.409097666	.741520320

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
5.721738267	.000000390	24570.219247100

Round 2

	<u>N</u> 60	
Mean	165.456500000	394.288916666
Variance	26227.254419600	547322.456933000

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.704076623	.548111921	.812723476

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
7.550917517	.000000000	84356.387672500

Hi-Vols

BaP (Method 2) vs. BaP (Method 3)

<u>Round 1</u>			
	<u>Method 2</u>	<u>N</u> 60	<u>Method 3</u>
Mean	12.273500000		15.536000000
Variance	203.091979067		213.678682033
	<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
	.535841309	.326265292	.695207288
<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>	
4.833300233	.000010238	111.625437966	

<u>Round 2</u>			
		<u>N</u> 60	
Mean	19.429666666		38.076833333
Variance	369.117382937		4592.268052500
	<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
	.558288177	.354588190	.711395409
<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>	
5.124824865	.000003569	726.865900620	

Hi-Vols
BaP (Method 2) vs. BaP (Method 4)

Round 1

	<u>Method 2</u>	<u>N</u> 60	<u>Method 4</u>
Mean	12.273500000		28.001500000
Variance	203.091979067		709.433155338

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.581666030	.384488598	.728083970

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
5.445888424	.000001093	220.788184491

Round 2

		<u>N</u> 60
Mean	19.338000000	58.850666666
Variance	366.160131525	14403.188575800

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.479427830	.256707507	.653796894

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
4.160541638	.000106335	1101.001960670

Personals

14 PNA's vs. 6 TPC's from Method 2

Round 1

	<u>14 PNA's</u>	<u>N</u> 122	<u>6 TPC's</u>
Mean	35.420491803		22.726229508
Variance	2174.042469170		875.907405495
	<u>Correlation</u>	<u>95% Lower Confidence Limit for Correlation</u>	<u>95% Upper Confidence Limit for Correlation</u>
	.931435534	.903216691	.951635767

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
28.038434968	.000000000	1285.333755580

Round 2

		<u>N</u> 120	
Mean	50.632500000		29.176666666
Variance	3691.593808820		1077.962644250
	<u>Correlation</u>	<u>95% Lower Confidence Limit for Correlation</u>	<u>95% Upper Confidence Limit for Correlation</u>
	.959435730	.942225768	.971594114

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
36.967454623	.000000000	1913.924042010

Personals

B.S. vs. BaP from Method 3

Round--1

	<u>B.S.</u>	<u>n</u> 144	<u>BaP</u>
Mean	1.151674305		13.728179166
Variance	1.664856331		436.243779351

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.563699506	.440736302	.665896711

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
8.132467288	.000000000	15.191500043

Round--2

	<u>n</u> 148	
Mean	2.148506756	8.838891891
Variance	6.138952632	396.028669796

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.635214436	.527956613	.722526850

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
9.937808192	.000000000	31.320653476

Horizontal Elutriator

14 PNA's vs. 6 TPC's from Method 2

Round 1

	<u>14 PNA's</u>	<u>N</u> 20	<u>6 TPC's</u>
Mean	106.308000000		77.270000000
Variance	9760.885480000		4614.940105260

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.992900530	.981728733	.997250911

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
35.414917412	.000000000	6663.975410520

Round 2

		<u>N</u> 18
Mean	118.750555555	62.877777777
Variance	10921.430370200	3086.333535940

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.869026507	.676654538	.950338179

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
7.025764356	.000002863	5045.383854240

Horizontal Elutriator
B.S. vs. BaP from Method 3

<u>Round 1</u>		
	<u>BaP</u>	<u>N</u>
		10
Mean	17.933000000	2.580000000
Variance	299.384312222	9.257333333

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.934458802	.740457922	.984722045

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
7.422807921	.000074552	49.194622222

<u>Round 2</u>		
		<u>N</u>
		9
Mean	19.072222222	2.944444444
Variance	278.998269443	5.992777777

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.883769324	.531618608	.975407997

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
4.997050088	.001570488	36.137138888

Horizontal Elutriator
B.S. vs. 14sPNA's from Method 2

Round 1

	<u>14 PNA's</u>	<u>N</u> 10	<u>B.S.</u>
Mean	75.362000000		1.280000000
Variance	3085.810395550		.748444444

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.725702581	.176752679	.930290946

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
2.983388609	.017509642	34.875711111

Round 2

		<u>N</u> 8	
Mean	105.635000000		3.412500000
Variance	13870.618428500		2.089821428

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.358510902	-.463326738	.848813164

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
.940701396	.383170374	61.038642857

Horizontal Elutriator
B.S. vs. 6 TPC's from Method 2

Round 1

	<u>6 TPC's</u>	<u>N</u> 10	<u>B.S.</u>
Mean	60.590000000		1.280000000
Variance	1826.501000000		.748444444

<u>Correlation</u>	<u>95% Lower Confidence Limit for Correlation</u>	<u>95% Upper Confidence Limit for Correlation</u>
.712487619	.150115480	.926512808

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
2.871972781	.020765913	26.343111111

Round 2

		<u>N</u> 8
Mean	47.771250000	3.412500000
Variance	1393.801069640	2.089821428

<u>Correlation</u>	<u>95% Lower Confidence Limit for Correlation</u>	<u>95% Upper Confidence Limit for Correlation</u>
.436819130	-.387132143	.872869950

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
1.189466670	.279187447	23.575267857

Gross (S&G)

14 PNA's vs. 6TPC's from Method 2

Round 1

	<u>14 PNA's</u>	<u>N</u> 20	<u>6 TPC's</u>
Mean	91.219500000		62.220000000
Variance	10211.029405000		4253.338526310

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.988487884	.970475175	.995536170

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
27.718425774	.000000000	6514.350010520

Round 2

		<u>N</u> 18
Mean	116.377777777	60.923888888
Variance	11119.315453500	2940.644048680

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.944430879	.854170335	.979444449

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
11.492569866	.000000003	5400.456015020

Gross (S&G)

B.S. vs. BaP from Method 3

Round 1

	<u>BaP</u>	<u>N</u> 10	<u>B.S.</u>
Mean	25.682000000		3.440000000
Variance	534.192973333		11.049333333

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.818369652	.389237761	.955618595

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
4.027719476	.003800096	62.873355555

Round 2

		<u>N</u> 9
Mean	19.131111111	3.411111111
Variance	304.814336110	4.973611111

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.489030368	-.259472493	.870493440

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
1.483322304	.181555842	19.040986111

Gross (S&G)

B.S. vs. 14 PNA's from Method 2

Round 1

	<u>14 PNA's</u>	<u>N</u> 10	<u>B.S.</u>
Mean	75.749000000		2.660000000
Variance	6714.570921110		3.358222222

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.383033039	-.325109766	.815946899

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
1.172827117	.274601595	57.517511111

Round 2

		<u>N</u> 8
Mean	93.870000000	3.875000000
Variance	9536.538771420	4.393571428

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.791278194	.195573618	.960440280

<u>Test for r=0 t-value</u>	<u>Test for r=0 Probability</u>	<u>Covariance</u>
3.169854968	.019322308	161.969571428

Gross (S&G)

B.S. vs. 6 TPC's from Method 2

Round 1

	<u>6 TPC</u>	<u>N</u> 10	<u>B.S.</u>
Mean	56.500000000		2.660000000
Variance	3170.226666660		3.358222222

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.468572335	-.228607963	.848058900

<u>Test for r=0</u> <u>t-value</u>	<u>Test for r=0</u> <u>Probability</u>	<u>Covariance</u>
1.500209416	.171950203	48.347777777

Round 2

		<u>N</u> 8
Mean	49.771250000	3.875000000
Variance	2075.120355350	4.393571428

<u>Correlation</u>	95% Lower Confidence Limit for <u>Correlation</u>	95% Upper Confidence Limit for <u>Correlation</u>
.781183064	.170016387	.958336618

<u>Test for r=0</u> <u>t-value</u>	<u>Test for r=0</u> <u>Probability</u>	<u>Covariance</u>
3.065022734	.022082393	74.590464285

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
HEALTH SERVICES AND MENTAL HEALTH ADMINISTRATION
National Institute For Occupational Safety And Health

TO : Kathleen A. Schulte, Chemist
Physical and Chemical Analysis Branch, DLCD

DATE: February 14, 1973

FROM : Richard W. Hornung
Mathematical Statistician
Statistical Services Section, DLCD

SUBJECT: Determination of sampling and analytical errors in data from Coal Tar Pitch Volatiles Study.

Introduction

One of the primary purposes of the study on Coal Tar Pitch Volatiles is determination of sampling error and analytical error. The large volume of data collected at five steel plants on two different sampling cycles contained no replication of sampling or analytical techniques. In this case, the only estimate of error available was extracted from a pooling of higher order interactions between factors in the experimental design. With the introduction of this newer collection of data with replicate samples, a better estimate of total error can be obtained. However, each analytical method was only performed once on each sample. Therefore, the analytical error will still be confounded with the sampling error. Nevertheless, by making comparisons of analyses performed on the same sample, it is possible to infer which analytical techniques have the largest error.

Statistical Analysis

In every case a natural log transformation was made on the data to stabilize the variances. This was done since the variances appeared to increase as the magnitude of the data values increased. The data with two replications was collected using cassettes containing glass fiber filters with silver membrane back-ups. This was analyzed by means of a two-factor analysis of variance. The first factor was coking conditions at 18 levels and the second factor was coking time at 3 levels. This resulted in 54 degrees of freedom for the error estimate, one for each pair of samples. As mentioned before this is an estimate of the error contributed by both sampling and analytical method. This type of analysis was done separately on three types of chemical analyses: Benzene soluble extract, BaP (Method 3) and the six TPC total from Method 2. A similar two-factor analysis was performed on the data which contained three replications on samples taken by the Door-Oliver cyclone. In this design the first factor was coking condition at 3 levels and coking time at 3 levels. This was a smaller data set, and consequently there were only 17 degrees of freedom for estimation of error. One degree of freedom was lost due to a missing data value which was replaced by the mean of the two observed values in that cell. This analysis also was used for each of the three analytical methods.

By comparing the error estimate for the data set with two replicates with that of the data set with three replicates, we can obtain some idea of the consistency of the estimates. A Bartlett's test for homogeneity of variance was performed on the pair of data sets associated with each of the three analytical methods. These tests showed no significant difference between the error estimates. The error estimates from each data set were not pooled since each was collected by means of a different sampling method. In all cases the two factors in the experimental design were found to have highly significant effects. This result will not be examined in any detail in this report since the primary concern is estimation of error. When information is received characterizing the individual coking conditions, a detailed examination of this factor will be made.

Summary of Results

The analyses indicate that the error variance for analyses of the benzene soluble extract is significantly lower than that for the 6 TPC totals (method 2) or BaP (method 3). A Bartlett's test comparing variances over the three analytical methods supports this statement. For each of the three methods, a Bartlett's test between the variances of the cassette samples (2 replicates) and the Door-Oliver samples (3 replicates) implied that there was no real difference. This is an indication that sampling errors do not differ significantly from one sampling method to another. In addition, because of the large differences in variance among different analyses performed on the same samples, it seems reasonable to assume that the largest contribution to error in this study was made by the chemical analysis. All the above results are tabulated on an attached page.

One further point should be made. Although the Benzene soluble analysis has the smallest error, you have stated that it is very sensitive to changes in humidity in the laboratory. The data analyzed in this report were obtained from chemical analysis performed during the summer months when humidity can be maintained at a constant level. Therefore, the benzene soluble method used during the dryer winter months may be subject to an increase in error. If this method is used it would be statistically advantageous to record periodic humidity readings.

If you need any further information, I am available at Ext. 3140.

Richard W. Hornung
Richard W. Hornung

cc: Dr. Edward J. Fairchild, II
Mr. John M. Bryant
Mr. Kenneth A. Busch
Mr. John V. Crable
Mr. Jerome Flesch
Mr. Jeremiah R. Lynch

ANOVA I
Analytical Method - Benzene soluble (Method 1)
Sampling Method - Cassette (2 reps)

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>M.S.</u>	<u>F</u>	<u>P</u>
Coking Conditions	17	29.8742	1.7573	186.448	.0000
Coking Times	2	.8140	.4070	43.184	.0000
Interaction	34	19.8559	.5840	61.962	.0000
Error	54	.5089	.0094		

Standard Deviation (% of Mean) = 10.2% 95% Confidence Limits = 8.6% to 12.6%

ANOVA II
Analytical Method - 6TPC Total (Method 2)
Sampling Method - Cassette (2 reps)

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>M.S.</u>	<u>F</u>	<u>P</u>
Coking Conditions	17	17.9152	1.0538	12.395	.0000
Coking Times	2	61.3731	30.6866	360.925	.0000
Interaction	34	24.3507	.7162	8.424	.0000
Error	54	4.5912	.0850		

Standard Deviation (% of Mean) = 33.8% 95% Confidence Limits = 27.8% to 42.9%

ANOVA III
Analytical Method - BaP (Method 3)
Sampling Method - Cassette (2 reps)

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>M.S.</u>	<u>F</u>	<u>P</u>
Coking Conditions	17	24.8759	1.4633	17.662	.0000
Coking Times	2	25.1559	12.5780	151.818	.0000
Interaction	34	22.8148	.6710	8.099	.0000
Error	54	4.4738	.0828		

Standard Deviation (% of Mean) = 33.8% 95% Confidence Limits = 27.4% to 42.3%

ANOVA IV
Analytical Method - Benzene Soluble
Sampling Method - Door-Oliver (3 reps)

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>M.S.</u>	<u>F</u>	<u>P</u>
Coking Conditions	2	3.5723	1.7862	101.489	.0000
Coking Times	2	1.3795	.6897	39.188	.0000
Interaction	4	14.3416	3.5854	203.716	.0000
Error	17	.2999	.0176		

Standard Deviation (% of Mean) = 14.2%

95% Confidence Limits = 10.2% to 21.3%

ANOVA V
Analytical Method - 6 TPC Total (Method 2)
Sampling Method - Door-Oliver (3 reps)

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>M.S.</u>	<u>F</u>	<u>P</u>
Coking Conditions	2	1.6288	.8144	18.819	.0000
Coking Times	2	13.5449	6.7724	156.499	.0000
Interaction	4	9.4137	2.3534	54.351	.0000
Error	17	.7357	.0433		

Standard Deviation (% of Mean) = 23.1%

95% Confidence Limits = 16.4% to 35.4%

ANOVA VI
Analytical Method - BaP (Method 3)
Sampling Method - Door-Oliver (3 reps)

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>M.S.</u>	<u>F</u>	<u>P</u>
Coking Conditions	2	1.7521	.8760	9.045	.0021
Coking Times	2	1.5267	.7634	7.882	.0038
Interaction	4	17.1186	4.2797	44.188	.0000
Error	17	1.6465	.0969		

Standard Deviation (% of Mean) = 36.5%

95% Confidence Limits = 25.5% to 57.4%

Table of Results of Bartlett's Tests for
Cassette Samples (54 d.f.) and Door-Oliver Samples (17 d.f.)

<u>Benzene Soluble</u>				
<u>Variances</u>	<u>d.f.</u>	<u>χ^2</u>	<u>d.f.</u>	<u>Probability</u>
.0094	54	2.2478	1	.1338
.0176	17			

<u>6 TPC Total (Method 2)</u>				
<u>Variances</u>	<u>d.f.</u>	<u>χ^2</u>	<u>d.f.</u>	<u>Probability</u>
.0850	54	2.9630	1	.0852
.0433	17			

<u>BaP (Method 3)</u>				
<u>Variances</u>	<u>d.f.</u>	<u>χ^2</u>	<u>d.f.</u>	<u>Probability</u>
.0828	54	.0631	1	.8016
.0969	17			

<u>Bartlett's Test for Equality of Variance Across the Three Analytical Methods</u>				
<u>Variance</u>	<u>d.f.</u>	<u>χ^2</u>	<u>d.f.</u>	<u>Probability</u>
.0094	54			
.0850	54	60.885	2	.0000*
.0828	54			

*Highly significant difference

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
HEALTH SERVICES AND MENTAL HEALTH ADMINISTRATION
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

TO : Kathleen A. Schulte, Chemist
Physical and Chemical Analysis Branch

DATE: March 29, 1973

FROM : Mathematical Statistician
Statistical Services, DLCD

SUBJECT: Correlations between trace metal concentrations and coal tar pitch volatile concentrations determined by several chemical analytical methods.

Introduction.

Per our discussion of March 21, 1973 a series of correlation coefficients was computed relating trace metal concentrations to chemical concentrations measured by analytical methods used in conjunction with the Coal Tar Pitch Volatile Study. The sum of the concentrations of five trace metals - Cr, Cu, Mn, Ni, and Zn - was correlated with the coal tar pitch volatile concentrations associated with each of four chemical analytical methods. These four methods are 1) Benzene soluble extract, 2) Gas chromatography, 3) Thin layer chromatography and 4) Liquid column chromatography. Data were available from two rounds of sampling, yielding a total of eight correlations to be computed.

Results.

The correlation coefficients resulting from these eight combinations were uniformly low. Only two of the eight were found to be significantly different from zero as a result of a Student's t-test. The largest of these two coefficients, and the highest of all those obtained, had a relatively low value of .2841. The variances of each sample were very high which is an indication that poor data may have contributed to the lack of correlation. However, these extremely low correlation coefficients lend little hope to the conjecture that more accurate measurements would result in substantially higher correlations. Numerical results for each combination are tabulated on the attached pages.

Richard W. Hornung
Richard W. Hornung

cc:
Dr. Edward J. Fairchild, II
Mr. John M. Bryant
Mr. John V. Crable
Mr. Jeremiah R. Lynch
Dr. Alexander Teass
Mr. Kenneth A. Busch

TRACE METAL TOTAL VS. BENZENE SOLUBLE

	Round 1 N = 57		Round 2 N = 59	
	<u>Mean</u>	<u>Variance</u>	<u>Mean</u>	<u>Variance</u>
Trace Metal	9.2873	23.8164	15.6508	97.8166
Benzene Soluble	1.6025	1.6642	3.2285	25.1689
Correlation	0.1457		.2705	
95% Confidence Limits	-.1194 to .3915		.0155 to .4925	
Student's t-test for $r = 0$ -- Probability	.2794		.0382	

TRACE METAL TOTAL VS. 14PNA TOTAL (METHOD 2)

	Round 1 N = 57		Round 2 N = 59	
	<u>Mean</u>	<u>Variance</u>	<u>Mean</u>	<u>Variance</u>
Trace Metal	9.2833	23.8194	15.6508	97.8166
14PNA Total	142.0477	61324.4269	176.9168	26967.9553
Correlation	.1119		.2841	
95% Confidence Limits	-.1531 to .3620		.0302 to .5036	
Student's t-test for $r = 0$ Probability	.4070		.0292	

TRACE METAL TOTAL VS. BaP (Method 3)

	Round 1 N = 57		Round 2 N = 59	
	<u>Mean</u>	<u>Variance</u>	<u>Mean</u>	<u>Variance</u>
Trace Metal	9.2837	23.8164	15.6508	97.8166
BaP (Method 3)	15.8309	222.9410	36.2066	4458.0241
Correlation	.0214		.2081	
95% Confidence Limits	-.2406 to .2804		-.0507 to .4408	
Student's t-test for $r = 0$ Probability	.8745		.1137	

TRACE METAL TOTAL VS. 9 PNA TOTAL (METHOD 4)

	Round 1 N = 57		Round 2 N = 59	
	<u>Mean</u>	<u>Variance</u>	<u>Mean</u>	<u>Variance</u>
Trace Metal	9.2837	23.8164	15.6508	97.8166
9 PNA Total (Method 4)	189.5223	41076.1276	381.0941	500394.5625
Correlation	.1335		.1918	
95% Confidence Limits	-.1317 to .3805		-.0677 to .4269	
Student's t-test for $r = 0$ Probability	.3222		.1456	

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
HEALTH SERVICES AND MENTAL HEALTH ADMINISTRATION
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

TO : John V. Crable
Chief, Physical & Chemical Analysis Branch, DLCD
Kathleen A. Schulte
Chemist, Physical & Chemical Analysis Branch, DLCD

DATE: April 12, 1973

FROM : Mathematical Statistician
Statistical Services Section, DLCD
Through: Kenneth A. Busch, Chief, Statistical Services Section, DLCD

SUBJECT: Report on statistical analysis of coal-tar pitch volatile data from Union Carbide contract.

This is the third and final report on the results of the statistical analysis of data from the Union Carbide contract concerning concentrations of coal-tar pitch volatiles in steel plants. It contains estimates of the error associated with different types of air sampling techniques and chemical analysis methods. In addition, the average chemical concentrations associated with the different levels of the factors in the analysis have been tabulated.

If there are any further questions or if there are additional areas that you would like to investigate please don't hesitate to call.

Richard W. Hornung

Richard W. Hornung

CC:

Dr. Edward J. Fairchild, II
Mr. John M. Bryant
Mr. Jeremiah R. Lynch
Mr. Jerome P. Flesch
✓ Dr. Alexander Teass

*STATISTICAL ANALYSIS OF LEVELS OF COAL-TAR
PITCH VOLATILES IN STEEL PLANTS*

Data Taken From Union Carbide Contract - No. HSM-099-71-7

*by
Richard W. Hornung
Mathematical Statistician
Statistical Services Section
Division of Laboratories and Criteria Development*

April 12, 1973

*for
Physical and Chemical Analysis Branch
John V. Crable, Chief,
Kathleen A. Schulte, Chemist*

Introduction:

The purpose of this report is to present the findings of a statistical analysis of data received through the Union Carbide contract on Coal Tar Pitch Volatiles. Two previous reports have been produced dealing with correlations of certain analytical methods used by the contractor and estimation of total error from replicated samples. The objectives of this analysis are threefold:

- 1) Estimation of error associated with sampling methods and chemical analyses.
- 2) Determination of the statistical significance of differences in means associated with the levels of the factors in the analysis.
- 3) Estimation of these means including statistical confidence limits.

Due to a lack of replication in the original experimental design the first objective (estimation of error) may be the least accurate. A more detailed explanation of this matter will be given later in the report.

Background:

The program for sampling included two one-week sampling periods at each of the five steel plants listed below.

- 1)
- 2)
- 3)
- 4)
- 5)

One cycle of sampling was done in the spring of 1971 and the other in the winter of 1972. Two types of samplers were used: fixed area (stationary) and personal samplers worn by employees. The fixed sampler contained seven different sampling devices of which six will be considered in this report. They are:

A. Respirable

- 1) Door-Oliver cyclone
- 2) British Cast Iron Research Association (BCIRA) cyclone
- 3) Horizontal Elutriator

B. Gross

- 1) Gross glass filter
- 2) Gross silver filter

C. High Volume sampler

Because of obvious differences in the volume of air sampled by types A, B, and C separate analyses were performed for each type.

In most cases these fixed samplers were positioned in three locations in each plant:

- 1) Larry car
- 2) Catwalk - push side
- 3) Catwalk - coke side

In a few instances where two catwalks were not available, two sampling packages were placed on one catwalk. There were three locations for personal samplers, grouped according to the individual's proximity to the discharge of gases from the oven. These were:

- 1) Oven top (Lidman, Larrycar operator, Tar chaser, Heater and Luterman)
- 2) Side of oven (Benchman, Door cleaner, Jamb cleaner, Door machine operator)
- 3) Further away from oven (Pushcar operator, Quench car operator, Wharfman)

These are the primary factors that contributed to formulation of the mathematical models used in the statistical analysis.

Mathematical Model.

After careful consideration and some useful suggestions by Mr. Jeremiah Lynch, a list was compiled containing factors expected to influence the response of the data. They are listed as follows accompanied by the symbol used for the average effect of that factor in the analysis.

- 1) Sampling Cycles - C_i $i = 1, 2$.
- 2) Steel Plants - P_j $j = 1, \dots, 5$.
- 3) Locations within Plants - L_k $k = 1, 2, 3$, or $1, 2$.
- 4) Sampling Days - $D_{1(ij)}$ $1 = 1, 2$ or $1, \dots, 4$.
- 5) Analytical Methods - M_m $m = 1, 2, 3$.
- 6) Sampling Methods - S_n $n = 1, 2$.

Not all of these factors were used in each analysis, although 1) and 2) were present in every case.

There were two basic statistical designs used - one for fixed samples and another for personal samples. There is one basic mathematical model which is slightly modified to fit individual cases. The design for the fixed samples is balanced (equal cell sizes) while the design for the personal samplers is unbalanced (unequal or blank cells). The following is the general model used,

$$y_{ijkl} = \mu + C_i + P_j + D_{l(ij)} + L_k + (CP)_{ij} + (CL)_{ik} + (PL)_{jk} \\ + (CPL)_{ijk} + (LD)_{kl(ij)} + \beta X_{ijkl} + 1_{ijkl}$$

where y_{ijkl} is the chemical concentration for the i th cycle, j th plant, k th location within the plants and the l th day for each cycle-plant combination. The remaining terms represent interactions between the main factors, while the βX_{ijkl} term is the product of the covariate and its regression coefficient. In all balanced designs used in this study there is only one data point in each $ijkl$ cell. The only deviation from this model is the addition, in a few cases, of one extra factor - either Analytical Methods or Sampling Methods - or a change in the number of levels of the Locations or Days factors.

The basic unbalanced design, used for data obtained from personal samples, is similar with one notable exception. The response variable is now y_{ijkln} and the term accountable to random analytical error is now e_{ijkln} , where the subscript n represents the number of data points within each $ijkl$ cell. In the unbalanced case n varies from cell to cell and may even be zero (blank cell).

The analysis of variance was computed in order to determine which of the factors in the model significantly affect the response, i.e. which of the terms in the model are different from zero.

The response variable in the model, y_{ijkl} , was the concentration of chemicals measured by Union Carbide. The contractor used seven different chemical analytical techniques in supplying the data. Data from only four of these analytical methods have been designated for statistical analysis. They are listed below including the chemicals that they measure.

Method 1: Benzene Soluble extract (mg/m³)

Method 2: Gas chromatography for polynuclear aromatic compounds (PNA's)

1) Fluoranthene	μg/m ³
2) Pyrene	"
3) Benz (a) anthracene	"
4) Chrysene	"

5) Benzo(a)pyrene	$\mu\text{g}/\text{m}^3$
6) Benzo(e)pyrene	"
7) Benz(c)acridine	"
8) Benz(a)anthrone	"
9) Benzo(b)fluoranthene	"
10) Benzo(j)fluoranthene	"
11) Benzo(k)fluoranthene	"
12) Dibenzo(a,h)anthracene	"
13) Anthanthrene	"
14) Benzo(g,h,i)perylene	"

Method 3: Thin-layer chromatography for Benzo(a)pyrene ($\mu\text{g}/\text{m}^3$)

Method 4: Liquid column chromatography for 9 PNA's

1) Pyrene	$\mu\text{g}/\text{m}^3$
2) Fluoranthene	"
3) Chysene	"
4) Benz(a)anthracene	"
5) Benzo(a)pyrene	"
6) Benzo(e)pyrene	"
7) Benzo(k)fluoranthene	"
8) Perylene	"
9) Anthanthrene	"

Having identified the response variables and controlled factors, the possible existence of uncontrolled factors (covariates) was examined. After a series of consultations with Mr. Lynch, Mr. Jerome Flesch of Hazard Evaluations Services Branch, DTS, and Mr. Joseph Seta of Industrial Hygiene Services Branch, DTS, the addition of a covariate to the model was considered appropriate. The uncontrolled factor possibly affecting the response was wind velocity and direction. Measurements were taken hourly every day at each plant sampled. In order to express both velocity and direction using only one term a vector approach was used. The wind speed was multiplied by the cosine of the angle which the direction formed with the sampling packages. The measurement was positive if the wind was blowing the volatile matter toward the samplers, and negative if it carried the fumes away from the sampling package.

Since in most cases the response variable (chemical concentrations) differed according to which analytical method was employed, several distinct statistical analyses were performed. With the help of Mr. Lynch a list of nine such analyses were compiled. These included the following, broken down into fixed and personal samplers:

Fixed Samplers:

- 1) Benzene soluble extract - gross samplers
- 2) Benzene soluble extract - respirable samplers
- 3) Total particulate - gross samplers
- 4) Total particulate - respirable samplers
- 5) BaP in Analytical Methods 2, 3, 4 - High Volume sampler
- 6) 6 TPC totals from Method 2

Personal Samplers:

- 1) Benzene soluble extract
- 2) Total particulate
- 3) 6 TPC totals from Method 2

The data collected by means of gross samplers was pooled by averaging the response from Gross silver filters and Gross glass filters. Respirable responses were taken as the average of data from the Door-Oliver, Horizontal Elutriator and BCIRA cyclones. Gross and respirable samples were then analyzed separately because of pronounced differences in the amount of particulate collected. For the same reason, High-Volume data was analyzed separately from that of gross and respirable samples.

Statistical Analysis and Results:

A) Covariate: Wind vector.

The statistical analysis using the wind vector as a covariate was computed for the first few cases considered. It soon became evident that the covariate was not contributing significantly to the observed response. This was evidenced by the high values for the probabilities associated with the F-test of the covariate in the analysis of variance (See Tables 1a - 1d). Therefore, for subsequent analyses the covariate was omitted in the interest of economy of time.

B) Log Transformation on the response variable.

After careful inspection of preliminary analyses, it became evident that a log transformation was necessary to stabilize the variance. The method of analysis of variance assumes a normal distribution with equality of variance in the cells. In this study higher variances accompanied the larger means, indicating that the variance would be best expressed as a percentage of the mean, which is the purpose of the log transformation.

Although nine different analyses appear to be somewhat combersome, they actually serve an important purpose. By examining the error estimates for each analysis,

the investigator has a criterion for comparing sampling methods and analytical techniques. A list of these error estimates for each analysis appears in Tables 3a and 3b, but a brief interpretation seems appropriate.

C) Error Estimates (Tables 3a and 3b).

The percentages listed under "Coefficient of Variation" in table 3a represent the per cent deviations from the mean represented by a distance of one standard deviation. The reason that percentages are used rather than rational number values is that the standard deviation increases as the mean increases, as mentioned earlier. When data is transformed by means of logarithms the standard deviations are generally expressed as coefficients of variation. Table 3b however, expresses the standard deviation in units of concentration because no log transformations were required with data obtained from personal samplers. In this case the variance was more stable as the means increased, so a log transformation was considered unnecessary. Nevertheless, it should be noted that the variance for the 6 TPC Total analysis is rather high. This is due to the fact that a total of six values was used as the response variable, thereby compounding the errors attributed to the chemical analyses. The error associated with any one of the six concentrations would not be nearly as high, but it is difficult to determine exactly from this analysis. Because of this high variance, the analysis of the 6 TPC Totals yielded few significant results since the mean differences associated with most of the factors in the model could be accounted for by random error.

Although the errors for the 6 TPC Totals analysis and the BaP analysis for analytical Methods 2, 3, and 4 are large, this is not necessarily an indication that these two analyses are unsuitable. As it turns out, the benzene soluble extraction is a preliminary step for the other three analytical methods. Therefore, since the benzene soluble fraction is the ingredient for further analysis by Methods 2, 3, and 4, the errors for these last three methods will include the error for the benzene soluble analysis. If we assume that the two errors are additive, it is necessary to subtract the benzene soluble error variance from the total error variance in any of the other three methods in order to arrive at a fair estimate of their error.

The analysis of variance for BaP measured by analytical Methods 2, 3, and 4 was broken down into three separate analyses, one for each method. The error for each of the three methods was then checked for homogeneity by a Bartlett's test. This resulted in the discovery that the three error variances could not be considered statistically different. This indicates that the overall pooled error for the BaP analysis is a good estimate of the error in each of the three methods. If we subtract the error contributed by the benzene soluble fraction we arrive at an estimate of the analytical error alone.

Expressed as an equation the relationship is:

$$\left[\sigma_S^2 + \sigma_{B.S.}^2 + \sigma_{2, 3, 4}^2 \right] - \left[\sigma_S^2 + \sigma_{B.S.}^2 \right] = \sigma_{2, 3, 4}^2$$

Total error for analysis of
BaP (Methods 2, 3, and 4)

Total error for
Benzene soluble
analysis

Analytical error
for Methods 2, 3
or 4

where: σ_S^2 = sampling error

$\sigma_{B.S.}^2$ = Benzene soluble error

$\sigma_{2, 3, 4}^2$ = Error for Methods 2, 3, or 4

The log variance for the statistical analysis on benzene soluble data obtained by the same High Volume Sampler has been calculated to equal .169. The log variance for the statistical analysis of BaP (Methods 2, 3, and 4) is equal to .251. Therefore by subtracting, taking the square root and the anti-log we arrive at a coefficient of variation for analytical technique equal to 33.1%.

Although this estimate is roughly one half of the total error for analytical methods 2, 3, and 4, it is important to remember that it does not include sampling error as do all other estimates. This error has been calculated purely to emphasize that errors associated with analytical techniques 2, 3, and 4 have been inflated by error from the benzene soluble technique. This error is not intended to be used for a comparison with other coefficients of variation listed in Table 3a.

The coefficient of variation for the statistical analysis of total particulate weights is an estimate of gross and respirable sampling error since no analytical technique was involved. However, once again a lack of replication made it necessary to obtain estimates by means of higher order interactions. Therefore, it is my feeling that these estimates may be somewhat larger than those that might be obtained by using replicate samples. This idea has been substantiated by the earlier (Feb. 14, 1973) analysis of certain replicated sampling methods.

The response variable for gross sample analysis of variance was an average of two values while the response variable for respirable sample analysis was an average of three values. Therefore, we must take this into account when comparing the error estimates. The mean square for the gross sample analysis is multiplied by 2 while the mean square for the respirable analysis is multiplied by 3. The corrected coefficient of variation is found in Table 3a for both the benzene soluble and total particulate statistical analyses.

Analysis of Variance Tables.

Tables 1a through 1f and Tables 2a through 2c list the pertinent results for the analyses of variance for fixed samples and personal samples, respectively. The column entitled "Source" lists all factors and their interactions for the particular analysis in question. The column headed "d.f." gives the degrees of freedom for each effect while the "F-value" column contains the numerical result of the F-test for equality of means at levels of the corresponding factor. The most important column is headed "Probability" since this is the criterion for determining which factors contain significantly different levels. The decimal fraction represents the probability that the observed differences in the means occur by chance alone. Any probability less than .05 has been designated as statistically significant in keeping with the usual statistical convention.

The factors consistently appearing significant are Plants and Locations (within each plant). In a few cases Sampling Cycle was significant but this was not consistent through out the series of nine analyses. The days on which samples were taken appeared significant, but since this is a random effect little can be done with this knowledge. A complete listing of the means of significant main effects and interactions (excluding Days) may be found in Tables 4a through 4i.

Duncan's Multiple Range Tests (Tables 4a - 4i).

All factors which showed significance in the analyses of variance were examined by means of Duncan's Multiple Range Tests. This is a test of all the means in any one factor utilizing all possible pairwise comparisons. The result is a determination of which means differ significantly from each other. Any group of means enclosed by brackets shows no significant differences among themselves. However, each bracket indicates a significant difference from any mean outside that bracket. 95% Confidence Limits are also supplied, serving as an upper and lower bound between which we can be 95% sure that the true mean lies.

Summary.

Because of the large number of exogenous factors affecting the response variable, the error in each statistical analysis was quite large. For this reason, and because of the lack of replication, a precise estimate of sampling error and analytical error was impossible. However, even though the total errors in all of the analyses were somewhat inflated, they allow us to make some comparisons between the different sampling methods and analytical techniques. Adopting this approach it would appear that respirable sampling methods have lower total error than the gross sampling methods (see Table 3a). It also appears that the benzene soluble technique has approximately the same error as analytical methods 2, 3, and 4, but

the total errors for methods 2, 3, and 4 are inflated because they contain the benzene soluble error. In addition, laboratory measurements have indicated that the benzene soluble technique is highly influenced by changes in humidity in the laboratory. This was not reflected in the present statistical analysis because all data grossly in error due to humidity was omitted. Therefore, it seems reasonable to suggest that other more stable methods be investigated in order to replace the benzene soluble method for extraction of the basic chemicals for analysis by techniques 2, 3, and 4.

The analysis of variance indicated that several factors were consistently significant. One such factor was the individual steel plants. In this case plant no. 2 and Plant No. 4 had significantly higher concentrations than the other three. In fact, Plant No. 4 often showed concentrations 4 or 5 times as high as the lowest of the other plants. Another significant factor was locations within the plant. Here it was found that the Larrycar location had about 2 times the PNA concentration of the catwalk locations. It is also interesting to note that the wind direction and velocity did not play an important role in raising or lowering concentrations. This is possibly due to the fact that the large number of standpipes around the ovens tend to act as a windbreak.

In the personal samples, the job location was highly significant. Those workers who spent a majority of their time on the oven top had on the order of two to three times the exposure of those in the next group (oven side).

In conclusion, I believe it is worth reiterating that much more accurate results could be obtained in further studies if replicate samples were taken and replicate analyses were performed. The difficulty of dividing a sample for replicate chemical analysis is a problem, but the possibility of artificially applying known equal concentrations of a given chemical to several filters might be investigated.

TABLE 1a
BENZENE SOLUBLE (RESPIRABLE)

<u>Source</u>	<u>d.f.</u>	<u>F-value</u>	<u>Probability</u>
Cycles - C_i	1	7.1837	.0231*
Plants - P_j	4	6.5259	.0075*
Locations - L_k	2	14.1185	.0002*
(CP) $_{ij}$	4	0.9203	.4893
(CL) $_{ik}$	2	1.8108	.1906
(PL) $_{jk}$	8	1.1816	.3597
(CPL) $_{ijk}$	8	1.7221	.1576
Days - $D_{l(ij)}$	10	3.4223	.0102*
Covariate	1	3.3409	.0833
(LD) $_{kl(ij)}$	19	MSE = .0891	used as error

TABLE 1b
BENZENE SOLUBLE (GROSS)

<u>Source</u>	<u>d.f.</u>	<u>F-value</u>	<u>Probability</u>
Cycles - C_i	1	1.7883	.2108
Plants - P_j	4	5.3634	.0143*
Locations - L_k	2	18.7328	.0001*
(CP) $_{ij}$	4	0.6714	.6198
(CL) $_{ik}$	2	0.1585	.8545
(PL) $_{jk}$	8	0.9776	.4822
(CPL) $_{ijk}$	8	1.5429	.2079
Days - $D_{l(ij)}$	10	2.0726	.0824
Covariate	1	1.4303	.2464
(LD) $_{kl(ij)}$	19	MSE = 0.1357	used as error

*shows significant difference at 5% level.

TABLE 1c
TOTAL PARTICULATE (RESPIRABLE)

<u>Source</u>	<u>d.f.</u>	<u>F-value</u>	<u>Probability</u>
Cycles - C_i	1	0.0409	.8411
Plants - P_j	4	7.6417	.0002*
Locations - L_k	2	18.0120	.0000*
(CP) $_{ij}$	4	0.4059	.8029
(CL) $_{ik}$	2	0.2692	.7649
(LP) $_{jk}$	8	1.5283	.1670
(CPL) $_{ijk}$	8	1.0858	.3857
Days - $D_{l(ij)}$	30	5.0975	.0000*
Covariate	1	.0109	.9172
(LD) $_{kl(ij)}$	59	MSE = .0824	used as error

TABLE 1d
TOTAL PARTICULATE (GROSS)

<u>Source</u>	<u>d.f.</u>	<u>F-value</u>	<u>Probability</u>
Cycles - C_i	1	3.4076	.0784
Plants - P_j	4	10.0395	.0001*
Locations - L_k	2	21.2476	.0000*
(CP) $_{ij}$	4	0.4538	.7688
(CL) $_{ik}$	2	0.1428	.8672
(LD) $_{jk}$	8	1.5900	.1474
(CPL) $_{ijk}$	8	1.5254	.1680
Days - $D_{l(ij)}$	30	2.6430	.0007*
Covariate	1	.7043	.4047
(LD) $_{kl(ij)}$	59	MSE = .1992	used as error

*shows significant difference at 5% level.

TABLE 1e
BaP, Analytical Methods 2, 3, and 4

<u>Source</u>	<u>d.f.</u>	<u>F-value</u>	<u>Probability</u>
Cycles - C_i	1	3.5982	.0675
Plants - P_j	4	6.1631	.0010*
Locations - L_k	2	1.6069	.2090
Analytical Method - M_n	2	38.7072	.0000*
(CP) $_{ij}$	4	1.6018	.1995
(CL) $_{ik}$	2	1.3603	.2644
(PL) $_{jk}$	8	2.0900	.0508
(CM) $_{in}$	2	0.2879	.7509
(PM) $_{jn}$	8	1.0563	.4055
(LM) $_{kn}$	4	1.8915	.1163
(CPL) $_{ijk}$	8	1.2783	.2719
(CPM) $_{ijn}$	8	0.4439	.8897
(CLM) $_{ikn}$	4	0.1105	.9786
(PLM) $_{jkn}$	16	1.3600	.1734
(CPLM) $_{ijkn}$	16	1.0952	.3672
Days - $D_l(ij)$	30	12.5543	.0000*
(LD) $_{kl(ij)}$	60	1.5929	.0159*
(MD) $_{nl(ij)}$	60	4.3873	.0000*
(LMD) $_{knl(ij)}$	120	MSE = 0.2511	used as error

*shows significant difference at 5% level.

TABLE 1f
6TPC Total

<u>Source</u>	<u>d.f.</u>	<u>F-value</u>	<u>Probability</u>
Cycles - C_i	1	0.3965	.5360
Plants - P_j	4	1.5941	.2147
Locations - L_k	1	0.3079	.5851
Sampling Methods - S_n	1	2.3137	.1439
(CP) $_{ij}$	4	1.0411	.4108
(CL) $_{ik}$	1	0.1632	.6905
(PL) $_{jk}$	4	1.1935	.3442
(CS) $_{in}$	1	5.1910	.0338*
(PS) $_{jn}$	4	0.7657	.5599
(LS) $_{kn}$	1	1.9036	.1829
(CPL) $_{ijk}$	4	0.4054	.8025
(CPS) $_{ijn}$	4	0.7458	.5722
(CLS) $_{ikn}$	1	0.0142	.9063
(PLS) $_{jkn}$	4	1.0045	.4285
(CPLS) $_{ijkn}$	4	0.3454	.8441
Days - $D_l(ijk)$	20	6.9032	.0001*
(SD) $_{nl(ijk)}$	20	MSE = 0.4310	used as error

*shows significant difference at 5% level.

TABLE 2a
Benzene Soluble (Personal)

<u>Source</u>	<u>d.f.</u>	<u>F-value</u>	<u>Probability</u>
Cycles - C_i	1	11.3664	.0030*
Plants - P_j	4	3.6004	.0229*
Locations - L_k	2	42.6867	.0000*
(CP) $_{ij}$	4	2.1778	.1085
(CL) $_{ik}$	2	1.1065	.2939
(PL) $_{jk}$	8	4.4419	.0007*
(CPL) $_{ijk}$	8	1.004	.4333
Days - $D_{l(ij)}$	20	1.7955	.0316*
(LD) $_{kl(ij)}$	40	1.1531	.2542
Error	262	MSE = 2.4033	

TABLE 2b
TOTAL PARTICULATE (PERSONAL)

<u>Source</u>	<u>d.f.</u>	<u>F-value</u>	<u>Probability</u>
Cycles - C_i	1	3.3382	.0827
Plants - P_j	4	11.5953	.0001*
Locations - L_k	2	96.5279	.0000*
(CP) $_{ij}$	4	2.2633	.0984
(CL) $_{ik}$	2	0.1015	.7501
(PL) $_{jk}$	8	6.1936	.0001*
(CPL) $_{ijk}$	8	0.6059	.6585
Days - $D_{l(ij)}$	20	1.2360	.2152
(LD) $_{kl(ij)}$	40	1.8107	.0199*
Error	545	MSE = 1.6574	

*shows significant difference at 5% level.

TABLE 2c
6TPC Total (Personal)

<u>Source</u>	<u>d.f.</u>	<u>F-value</u>	<u>Probability</u>
Cycles - C_i	1	1.5937	.2213
Plants - P_j	4	2.3431	.0898
Locations - L_k	2	57.3644	.0000*
(CP) $_{ij}$	4	2.3532	.0876
(CL) $_{ik}$	2	0.1252	.8824
(PL) $_{jk}$	8	3.7388	.0004*
(CPL) $_{ijk}$	8	0.4139	.9121
Days - $D_{l(ij)}$	20	1.238	.2394
(LD) $_{kl(ij)}$	40	0.6846	.9117
Error	264	MSE = 532.2280	

*shows significant difference at 5% level.

Tables of Error Estimates for All Analyses

TABLE 3a

<u>Analysis</u>	<u>Coefficient of Variation (% of the Mean)</u>	<u>95% Confidence Limits</u>
Benzene sol (respirable)	67.7%	48.1% to 112.6%
Benzene sol (Gross)	68.4%	48.6% to 113.9%
Total Particulate (respirable)	64.4%	51.9% to 82.2%
Total Particulate (Gross)	87.9%	70.1% to 114.2%
BaP - Methods 2, 3, 4	65.1%	56.11% to 77.71%
6TPC Total	92.8%	65.21% to 158.1%
Average C.V. for each of the six individual TPC's	30.7%	22.7% to 47.3%

TABLE 3b

<u>Analysis</u>	<u>Standard Deviation</u>	<u>Standard Deviation as % of Grand Mean</u>	<u>95% Confidence Limits</u>
Benzene soluble (personal)	1.5503	93.2%	1.4293 to 1.6972
Total Particulate (personal)	1.2874	87.1%	1.2158 to 1.3693
6TPC Total	23.0701	109.0%	21.2755 to 25.2476

Duncan's Multiple Range Tests for Pair-Wise Equality of
Means Among Significant Factors in Each Statistical Analysis

TABLE 4a
BENZENE SOLUBLE ANALYSIS (RESPIRABLE)

<u>PLANTS</u>	<u>Plant No.</u>	<u>n</u>	<u>Means (mg/m³)</u>	<u>95% Confidence Limits</u>
	1	12	1.2418	1.0488 to 1.4703
	3	12	1.5867	1.3401 to 1.8786
	5	12	1.8845	1.5917 to 2.2312
	2	12	2.7460	2.3193 to 3.2512
	4	12	6.0401	5.1014 to 7.1514

<u>LOCATIONS</u>	<u>Location No.</u>	<u>n</u>	<u>Means (mg/m³)</u>	<u>95% Confidence Limits</u>
	2	20	1.8352	1.6102 to 2.0917
	3	20	2.4698	2.1669 to 2.8150
	1	20	3.7945	3.3292 to 4.3248

TABLE 4b
BENZENE SOLUBLE ANALYSIS (GROSS)

<u>PLANTS</u>	<u>Plant No.</u>	<u>n</u>	<u>Means (mg/m³)</u>	<u>95% Confidence Limits</u>
	5	12	2.4468	1.9864 to 3.0138
	3	12	2.6853	2.1801 to 3.3076
	1	12	2.7223	2.2101 to 3.3532
	2	12	4.8400	3.9294 to 5.9616
	4	12	7.1765	5.8263 to 8.8395

<u>LOCATIONS</u>	<u>Location No.</u>	<u>n</u>	<u>Means (mg/m³)</u>	<u>95% Confidence Limits</u>
	2	20	2.7231	2.3171 to 3.2002
	3	20	3.1146	2.6502 to 3.6603
	1	20	6.0848	5.1776 to 7.0000

TE: Means enclosed by brackets are not significantly different

TABLE 4c
TOTAL PARTICULATE ANALYSIS (RESPIRABLE)

<u>PLANTS</u>	<u>Plant No.</u>	<u>n</u>	<u>Means (mg)</u>	<u>95% Confidence Limits</u>
	1	24	1.7916]	1.5972 to 2.0096
	5	24	2.1324]	1.9010 to 2.3919
	3	24	2.9328]	2.6146 to 3.2897
	2	24	5.2954]	4.7209 to 5.9399
	4	24	7.0166]	6.2553 to 7.8705
<u>LOCATIONS</u>	<u>Location No.</u>	<u>n</u>	<u>Means (mg)</u>	<u>95% Confidence Limits</u>
	2	40	3.1669]	2.8973 to 3.4615
	3	40	3.1905]	2.9189 to 3.4873
	1	40	5.1439]	4.7061 to 5.6225

TABLE 4d
TOTAL PARTICULATE ANALYSIS (GROSS)

<u>PLANTS</u>	<u>Plant No.</u>	<u>n</u>	<u>Means (mg)</u>	<u>95% Confidence Limits</u>
	5	24	5.8201]	4.8683 to 6.9579
	1	24	7.5734]	6.3349 to 9.0540
	3	24	11.5033]	9.6222 to 13.7522
	2	24	12.3262]	10.3105 to 14.7359
	4	24	25.3610]	21.2137 to 30.3191
<u>LOCATIONS</u>	<u>Location No.</u>	<u>n</u>	<u>Means (mg)</u>	<u>95% Confidence Limits</u>
	2	40	7.9711]	6.9414 to 9.1535
	3	40	10.8872]	9.4808 to 12.5022
	1	40	18.6919]	16.2774 to 21.4646

NOTE: Means enclosed by brackets are not significantly different.

TABLE 4e
BaP, Analytical Methods 2, 3, and 4 (Fixed)

<u>PLANTS</u>	<u>Plant No.</u>	<u>n</u>	<u>Means ($\mu\text{g}/\text{m}^3$)</u>	<u>95% Confidence Limits</u>
	1	72	9.1062]	8.1109 to 10.2233
	3	72	16.2560]	14.4792 to 18.2508
	5	72	20.8752]	18.5935 to 23.4369
	2	72	27.9464]	24.8919 to 31.3758
	4	72	68.0039]	60.5711 to 76.3489

<u>ANALYTICAL Methods</u>	<u>Method No.</u>	<u>n</u>	<u>Means ($\mu\text{g}/\text{m}^3$)</u>	<u>95% Confidence Limits</u>
	2	120	15.8053]	14.4499 to 17.2878
	3	120	26.0819]	23.8452 to 28.5284
	4	120	43.4252]	39.7012 to 47.4985

TABLE 4f
6 TPC Total (Fixed)

<u>CYCLE X SAMPLING METHOD INTERACTION</u>	<u>Interaction Subscript</u>	<u>n</u>	<u>Means ($\mu\text{g}/\text{m}^3$)</u>	<u>95% Confidence Limits</u>
	2, 2	20	50.8748]	41.1543 to 73.1696
	1, 1	20	62.2199]	46.6629 to 82.9635
	2, 1	20	70.6799]	53.0076 to 94.2440
	1, 2	20	77.2699]	57.9499 to 103.0311

NOTE: Means enclosed by brackets are not significantly different.

TABLE 4g
Benzene Soluble (Personal)

<u>CYCLES</u>	<u>Cycle</u>	<u>n</u>	<u>Means (mg/m³)</u>	<u>95% Confidence Limits</u>
	Spring	146	1.1602]	.9087 to 1.4117
	Winter	146	2.1681]	1.9166 to 2.4196

<u>PLANTS</u>	<u>Plant No.</u>	<u>n</u>	<u>Means (mg/m³)</u>	<u>95% Confidence Limits</u>
	5	57	0.8398]	.4373 to 1.2423
	3	59	0.9749]	.5793 to 1.3705
	1	60	1.6429]	1.2506 to 2.0352
	2	56	2.3131]	1.9071 to 2.7191
	4	60	2.5408]	2.1485 to 2.9331

<u>LOCATIONS</u>	<u>Location No.</u>	<u>n</u>	<u>Means (mg/m³)</u>	<u>95% Confidence Limits</u>
	3	86	0.6977]	.3700 to 1.0254
	2	110	1.3748]	1.0851 to 1.6645
	1	96	2.8616]	2.5515 to 3.1717

PLANT X LOCATION INTERACTION

<u>Plant No.</u>	<u>Location 1</u> <u>n</u>	<u>Mean (mg/m³)</u>	<u>Plant No.</u>	<u>Location 2</u> <u>n</u>	<u>Mean (mg/m³)</u>
5	16	1.0027]	3	17	.7334]
3	18	1.9172]	5	23	.9740]
1	20	1.9821]	2	17	1.0893]
4	21	4.2273]	1	30	1.5764]
2	22	4.3523]	4	23	2.1975]

NOTE: Means enclosed by brackets are not statistically different.

Table 4g
Benzene Soluble (Personal)

PLANT X LOCATION INTERACTION
(continued)

<u>Plant No.</u>	<u>Location 3</u> <u>n</u>	<u>Mean (mg/m³)</u>
3	24	.4392
5	18	.5235
4	16	.8207
2	17	.8980
1	11	1.0581

NOTE: Means enclosed by brackets are not statistically different.

TABLE 4h
Total Particulate (Personal)

<u>PLANTS</u>	<u>Plant No.</u>	<u>n</u>	<u>Means (mg)</u>	<u>95% Confidence Limits</u>
	1	112	0.6786]	.4402 to 0.9170
	5	114	1.0542]	.8179 to 1.2905
	3	119	1.4383]	1.2070 to 1.6696
	2	112	2.0508]	1.8124 to 2.2892
	4	118	2.1228]	1.8905 to 2.3551

<u>LOCATIONS</u>	<u>Location No.</u>	<u>n</u>	<u>Means (mg)</u>	<u>95% Confidence Limits</u>
	3	147	0.6803]	.4722 to .8884
	2	239	0.9959]	.8327 to 1.1591
	1	189	2.6957]	2.5122 to 2.8792

PLANT X LOCATION INTERACTION

<u>Plant No.</u>	<u>Location 1</u>	<u>Mean (mg)</u>	<u>Plant No.</u>	<u>Location 2</u>	<u>Mean (mg)</u>
	<u>n</u>			<u>n</u>	
1	34	1.0941]	1	54	.5432]
5	27	1.9707]	5	56	.8554]
3	40	2.4543]	2	42	.9548]
2	48	3.5056]	3	39	1.1038]
4	40	3.8160]	4	49	1.5847]

NOTE: Means enclosed by brackets are not significantly different.

TABLE 4h
Total Particulate (Personal)

PLANT X LOCATION INTERACTION
(continued)

<u>Location 3</u>		
<u>Plant No.</u>	<u>n</u>	<u>Mean (mg)</u>
1	24	.3950
5	31	.6152
4	29	.6966
3	40	.7485
2	23	.9269

NOTE: Means enclosed by brackets are not significantly different.

TABLE 4i
6 TPC Total (Personal)

<u>LOCATIONS</u>	<u>Location No.</u>	<u>n</u>	<u>Means ($\mu\text{g}/\text{m}^3$)</u>	<u>95% Confidence Limits</u>
	3	78	6.0205]	0.9006 to 11.1404
	2	121	12.4165]	8.3058 to 16.5272
	1	95	44.7337]	40.0945 to 49.3729

PLANT X LOCATION INTERACTION

<u>Plant No.</u>	<u>Location 1</u> <u>n</u>	<u>Mean ($\mu\text{g}/\text{m}^3$)</u>	<u>Plant No.</u>	<u>Location 2</u> <u>n</u>	<u>Mean ($\mu\text{g}/\text{m}^3$)</u>
1	15	22.7200]	2	23	4.2869]
5	12	26.3166]	1	28	5.7179]
3	23	42.5000]	3	14	10.9928]
2	26	47.7808]	5	31	14.3677]
4	19	72.2789]	4	25	25.7759]

<u>Plant No.</u>	<u>n</u>	<u>Mean ($\mu\text{g}/\text{m}^3$)</u>
1	17	4.3176]
4	14	4.5714]
2	10	5.4800]
3	22	7.4955]
5	15	7.5000]

NOTE: Means enclosed by brackets are not significantly different.