APPENDIX G

WORK PLAN FOR
REMOVAL ACTION - PHASE I

Combustion, Inc.
Denham Springs, Louisiana
6/30/92

AIR MONITORING PLAN
COMBUSTION, INC. REMOVAL ACTION

6/30/92

COMBUSTION, INC. SITE
DENHAM SPRINGS, LOUISIANA

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Air Monitoring Plan
Combustion, Inc. Removal Action

Combustion, Inc.
Denham Springs, Louisiana

SUMMARY

This plan describes the air monitoring activities to be conducted during the removal action (cleanup) of the Combustion, Inc. site. Air monitoring will provide a means of assessing the off site impact, if any, of cleanup activities and will provide a mechanism for triggering modification or discontinuation of operations.

Air monitoring will consist of continuous meteorological measurement and recording, daily monitoring for a broad group of volatile organic compounds and dust using field instrumentation and daily collection of air samples for laboratory analyses of specific volatile compounds (benzene, chlorobenzene, toluene, xylene, etc.). Monitoring will also include periodic collection and analyses of air samples for lead, PCBs and polynuclear aromatic (PNA) compounds.

The chemicals of primary concern during cleanup of the Combustion, Inc. site belong to the volatile group of compounds and include such chemicals as toluene, benzene, xylene and chlorinated solvents. There will be three levels of continuous monitoring for volatile chemical emissions during cleanup activities:

1. An organic vapor monitor (OVM) capable of detecting the volatile chemicals of concern present at the site will be used within the cleanup activity areas to monitor performance of the emission control devices and waste handling practices. This monitoring will be used to fine tune the control devices, to guide/limit waste handling practices and provide early warning of a release.

2. Additional organic vapor analyzers capable of detecting the organic vapors of concern will be in continuous use at the perimeters of the Process Area and Pond Area to immediately detect release of volatile chemicals. Organic vapor action levels have been set to trigger modification of waste handling practices at the Process Area or Pond Area and/or shut down of the process at the respective areas.

3. Air samplers will be placed upwind and downwind of the site at the nearest residences (or closer) for collection of samples for chemical specific laboratory analyses. The resulting data from this monitoring will be used to assess compliance with the DEQ set air standards for the project and to assure protection of the residential occupants. A minimum of two downwind samples will be collected at the Process Area and Pond Area at the nearest residences and analyzed during each day waste residuals are handled at the respective areas. Additional samplers will be available if wind is calm or transient.

   Downwind air samples will also be collected at the perimeters of the Process Area and Pond Area during each day waste residuals are handled at the respective areas. These samples will be analyzed, if necessary, to verify any offsite release, differentiate OVM readings into specific chemicals, and/or to modify the OVM action levels.

In addition to the above monitoring, field detection kits (Drager Tubes) specific to benzene, and/or toluene will be available onsite to check for the presence of these specific compounds in air on an as requested basis. These kits may be used in response to increased odor levels or residential complaints. These kits would be used in conjunction with the OVM instruments.

Chemicals present at the site but of a lesser concern relative to air emissions during cleanup include PCB's, polynuclear aromatic compounds (PNAs) and metals such as lead. These chemicals have relatively low volatility potential and emission of these chemicals during cleanup activities would primarily be through generation and wind dispersal of contaminated dust. The potential for generating contaminated dust when handling oily and/or wet wastes is low and control of dust emissions is easily performed.

Air samples for laboratory analyses of lead, PCBs and PNAs will be collected upwind and downwind of the site at the same offsite locations that the specific volatile compound samples are collected. Backup samples will also be collected at the perimeters of the Process Area and Pond Area as described for the volatile compound monitoring. Sampling for these compounds will be performed at the initiation of waste handling activities in the Pond Area (both Phase I and Phase II). Dust levels in air will be continuously measured with field instrumentation during work handling activities.

Average concentration limits for specific chemical compounds have been set by the Louisiana Department of Environmental Quality (DEQ). The basis for these average concentration limits considers the close proximity of residences, a two year project duration, predominant wind direction, a health-based risk assessment approach, and multiple factors of safety. If average specific chemical concentrations or field instrument readings exceed the average concentration limits set by the regulatory agencies, the cleanup activities will be stopped and/or modified to reduce emissions to acceptable levels.

1 - INTRODUCTION

This plan describes the air monitoring activities to be conducted during cleanup of the Combustion, Inc. site. Air monitoring will provide a means of assessing the off site impact, if any, of cleanup activities and will provide a mechanism for triggering modification or discontinuation of operations.

1.1 Background

The Combustion, Inc. site is an inactive waste oil recycling facility located in Livingston Parish, Louisiana, approximately three miles northeast of the city of Denham Springs. The site includes a processing area and a separate area approximately one half mile away that consists of a series of 14 shallow ponds. These two areas are referred to as the Process Area and the Pond Area respectively. An underground pipeline connects the two areas. The facility operated from the mid 1960's until 1982. Wastes on-site include used oil, water, a methanol and water mixture, tank bottom sediments, and pond bottom sediments. The primary site constituents include volatile organic compounds, semi-volatile organics, PCBs and heavy metals.

A Removal Action under the auspices of the Louisiana Department of Environmental Quality (DEQ) is proposed for the site. The proposed Removal Action will be conducted in two phases. Phase I of the Removal Action includes the removal and proper disposal of the aboveground and underground tanks and their contents, above ground structures, the pipeline connecting the Process Area to the Pond Area, and the oil on the surface of the ponds. Specific Removal Action activities will include pumping and loading of oil for disposal, possible on-site processing of the oil and tank bottoms, hydroblasting tanks, and removing underground tanks. Of these activities, on-site oil processing including the mixing, chemical addition and centrifuging have the greatest potential for air emissions because the oil must be heated from 150° to 170° Fahrenheit in a mix tank prior to centrifuging. When the process equipment is not operating (i.e., when movement, mixing, and/or heating of the oil stops) air emissions are anticipated to be equivalent to or less than current background levels. The need to process the oil will depend

on the quality of the oil and the requirements of the disposal facility. The need to process the oil will be determined following completion of waste profiling and contracting with the disposal facilities.

The technologies to be used for the Phase II Removal Action to address the Pond Area soils and sludges and buried materials in the Process Area have not yet been selected. Based on the characterization of the materials present at the site (as documented in the Preliminary Remedial Investigation Report revision dated March 30, 1990), it is anticipated that the potential air emissions from the Phase II Removal Action would be limited to volatile organic compounds and/or metals (made airborne as particulates). Thus, the monitoring program described herein is expected to adequately address both phases of the Removal Action. This plan will be revised as appropriate if it is determined that the Phase II Removal Action may emit constituents other than volatile organic compounds or particulate metals.

The Phase I and Phase II field activities are anticipated to require less than two years to complete. However, a two year time frame is used for establishing emission compliance levels.

2 - SAMPLING METHODOLOGIES

2.1 Volatile Organic Compounds

2.1.1 Real-time Monitoring

Emissions of volatile organic compounds (VOCs) on-site will be monitored using a direct reading instrument. A photoionization detector (PID) instrument such as the Thermo Environmental Model 580 B portable organic vapor monitor (OVM) or equivalent, will be used to continuously detect concentrations of organic vapors. The PID instrument is capable of detecting 0.1 to 2000 parts per million (ppm) total volatile organic compounds in air. Values obtained from two direct-reading PID instruments, one positioned upwind and one downwind of the Process Area and Pond Area fence lines will be compared to action levels to determine the need to modify or stop ongoing removal operations.

In addition to the site perimeter monitoring, a PID instrument will be used by the remediation contractor to evaluate the effectiveness and performance of emission control devices and to monitor emissions from waste handling procedures. The remediation contractor shall immediately report to the air monitoring personnel any readings greater than ten parts per million total hydrocarbons in the breathing zone exceeding a duration of five minutes.

Draeger Tube field detection kits specific to benzene and/or toluene will be available to check for the presence of these specific compounds in response to increased odor levels or residential complaints on an as requested basis. The samples will be collected using a hand operated pump. The draeger tubes will provide an immediate colorimetric indication of the presence of these compounds.

2.1.2 Integrated Sampling

EPA Method TO1 found in the "Compendium of Methods with the Determination of Toxic Organic Compounds in Ambient Air" (EPA-600/4-89-017, June, 1988) will also be used for the collection of samples to be analyzed for volatile organic compounds. In this method air is sampled through a sorbant tube containing Tenex^{R} adsorbent using a portable sampling pump such as the SKC Model 222-3 or equivalent. Following Tenex adsorption, thermal desorption is performed with GC/MS separation, detection and compound-specific identification. Samples will be analyzed for the compounds listed in Table 2-1, which are the compounds that have been detected in site materials and which can be detected using the TO1 method.

Samples will be collected during removal action activities that have the potential to emit VOCs to the air.

The use of Method TO1 provides continuous chemical-specific monitoring with low detection limits. This method will be utilized for compound-specific sampling at off site locations (where property access is allowed) and at the fence line. The method is capable of detecting individual chemicals in the low part per billion range depending on the sample volume.

2.2 Particulate Matter

2.2.1 Real-time Monitoring

A MINIRAM Model PDM-3 aerosol monitor will be used for real-time monitoring of particulate matter in the exclusion zone as an indicator for metals, PCBs and PNAs in the air. The MINIRAM is capable of detecting 0.01 mg/m^3 to 100 mg/m^3 total particulates in air. The instrument will be used to determine real-time air concentrations of dust during activities which have the potential for dust generation (e.g., excavation or chemical solidification/stabilization) during Phase I and Phase II of the Removal Action. Values obtained from two direct reading MINIRAM instruments positioned on stands upwind and downwind of the Process Area

TABLE 2-1

Compounds Detected at Combustion, Inc.
and Measured by
EPA Method TO1 Sample Analysis

Benzene

Chlorobenzene

Chloroethane

Chloroform

1,1-Dichloroethane

1,2-Dichloroethane

1,2-Dichloroethene

1,4-Dichlorobenzene

Ethyl benzene

Styrene

Tetrachloroethene

Toluene

Trichloroethene

Xylenes

and Pond Area sites will be compared to action levels to determine the need to modify or halt site activities.

2.2.2 Integrated Samples

The method in 40 CFR Part 50 Appendix G, "Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Air," will be used to collect and analyze air samples for lead. This method utilizes high volume air pumps at a flow rate of 20 to 60 cubic feet per minute to sample air through an 8 x 10 inch glass fiber filter. Samples will be collected using the General Metal Works Tripod GMWT 2200 Hi-Vol Air Sampler.

2.3 Polynuclear Aromatic Hydrocarbon Compounds (Integrated Samples)

The EPA Method TO13 found in the "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air" (EPA-600/4-89-017, June 1988) will be used for the collection of air samples to be analyzed for polynuclear aromatic hydrocarbon (PNA) compounds. In this method, air is sampled through a glass fiber filter and a cartridge containing polyurethane foam (PUF) and XAD-2 sorbant resin using a high volume sampling pump such as the General Metal Works PS-1 sampler or equivalent. Following sampling, analysis is accomplished using Soxhlet extraction with an appropriate solvent and High Performance Liquid Chromatography or GC/MS as appropriate. Samples will be analyzed for the compounds listed in Table 2-2.

The use of Method TO13 provides compound specific monitoring at low detection limits. This method will be utilized for compound specific receptor point and fence line sampling and is capable of detecting individual chemicals in the low part per billion range depending on exact sample volume.

Table 2-2

Compounds Detected at Combustion, Inc.
and Measured by
EPA Method TO13 Sample Analysis

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(e)pyrene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

2.4 Polychlorinated Biphenyls (Integrated Samples)

The EPA Method TO4 found in the "Compendium of Methods for the Determination of Toxic Organic compounds in ambient air" (EPA-600/4-89-017, June 1988) will be used for the collection of air samples to be analyzed for polychlorinated biphenyls. In this method, air is sampled through a glass fiber filter and a cartridge containing polyurethane foam (PUF) using a high volume sampling pump such as the General Metal Works PS-1 sampler or equivalent. Following sampling, analysis is accomplished using Soxhlet extraction with an appropriate solvent and gas chromatography with electron capture detection for PCBs.

The use of method TO4 provides PCB monitoring at low detection limits. This method will be utilized for receptor point and fence line sampling and is capable of detecting PCBs in the low part per billion range depending on sample volume.

2.5 Field Data Collection

Air monitoring field data will be collected and maintained on the form shown in Figure 2-1. Additional field sampling observations will be maintained in a field sampling notebook dedicated to the project.

2.6 Meteorological Data Collection

Meteorological data will be collected at a meteorological station set up at the site. Sensors for wind direction and wind speed will be three meters above the ground surface. Wind speed and wind direction monitors will be located in the Process Area and in the Pond Area. A rainfall recorder and temperature recorder will be located at the Process Area.

2.7 Quality Assurance/Quality Control

2.7.1 Sampling Instrument Calibration

Five different types of sampling instruments will require calibration for this air monitoring plan: the photoionization detectors, the low volume air pumps used to collect samples in the EPA TO1 method, MINIRAM particulate monitors, high-volume air pumps used to collect samples for the determination of lead in suspended particulates, PNAs and PCBs and PS-1 samplers.

Photoionization Detector Calibration Calibration of the Thermo Environmental Model 580B OVM will be as follows:

1. Remove the side plate on the right side of the OVM and turn on the main power switch; replace plate.

2. Turn on the "on/off" button on the top of the meter.

3. Push the "mode/store" button and the screen shows "log this value."

4. Push the "-" button and the screen shows "R/comm-Param" etc.

5. Push the "-" button and the screen shows "Free Space."

6. Push the "-" button and the screen shows "Reset to calibrate."

7. Push the "Reset" button and the screen shows "Restore backup" etc.

8. Push the "-" button and the screen shows "Zero Gas" etc.

COMB[illegible]N, I[illegible]ITE
AIR MONITORING DATA

Project No.:_____
Project Name:_____
Dates:_____
Sampler Signature:_____

Temperature:_____
Humidity:_____
Wind Speed:_____
Wind Direction:_____

SAMPLE NO.	SAMPLE STATION	SAMPLE DESCRIPTION	PUMP NO. OVN ID	RATE SCD L/min	RATE ECD L/min	AVERAGE RATE (L/min)	TIME ON	TIME OFF	ELAPSED TIME (min)	SAMPLE VOLUME (L)	TYPE OF TUBE OR FILTER	ID OR LOT	ANALYZE SAMPLE FOR	SUGG. METHOD	ACTIVITY

9. Attach charcoal scrubber poly fitting to the OVM and push the "Reset" button and wait until the screen shows "span ppm = 0100", then push the "+" button.

10. Remove charcoal scrubber and attach the calibration standard bottle with plastic tubing, then turn on the bottle.

11. Push the "Reset" button and wait until the screen shows "Reset to calibrate."

12. Push the "mode" button and turn off calibration standard and remove.

The OVMs will be calibrated every morning they will be used prior to the start of the day's activities. Periodic checks of the calibration will be made throughout each day to ensure accuracy of readings. OVM meter malfunctions or reading discrepancies will be noted and brought to the immediate attention of the field team leader. If faulty, the OVM meter will be removed from use until serviced and/or repaired.

Low Flow Pump Calibration Low flow sampling pumps will be calibrated before and after each day of sampling, using a high accuracy electronic bubble flow meter that provides instantaneous air flow readings and a cumulative averaging of multiple samples. These calibrators measure the flow rate of gases and present the results as volume per unit of time. A sample tube containing Tenex^{R} and designated for calibration purposes only will be used in-line during calibration. The calibration procedure is as follows:

1. Allow the pump to run five minutes prior to voltage check and calibration.

2. Assemble the Tenex^{R} tube to flexible Tygon^{R} tubing and attach to the pump outlet.

3. Connect the inlet of the Tenex^{R} tube to the top outlet of the calibration cell.

4. Visually inspect all Tygon[R] tubing connections.

5. Wet the inside of the electronic flow cell with the supplied soap solution by pushing the button several times.

6. Turn on the pump and adjust the pump rotameter to the appropriate flow rate setting.

7. Press the button on the electronic bubble meter. The meter will capture a single bubble and electronically time the bubble.

8. Repeat Step 7 twice. The instrument will automatically average the three numbers to produce an average flow rate. The average flow rate will be entered on the field form entitled Air Monitoring Data (Figure 2-1).

9. While the pump is still running, adjust the pump, if necessary.

10. Repeat the procedures described above for all pumps to be used for sampling. The same Tenex[R] tube may be used for all calibrations.

MINIRAM Calibration

The interior walls of the MINIRAM sampling chamber reflect a small amount of the light from the infrared source into the detector. This background level is referred to as the "zero value", and is automatically subtracted from all aerosol concentration readings during the measurement mode. The result is that the displayed readings depend only on the actual dust concentration present within the sensing chamber.

The zero value varies from instrument to instrument as well as with different sensing chambers. It will increase somewhat as the chamber inner walls and windows become contaminated with dust. A zero update should be performed after cleaning the sensing chamber. Processing ZERO during a measurement period provides momentary display of the stored zero concentration value used by the MINIRAM to correct all digital concentration readings (the analog output signal is not zero-corrected). To update the ZERO value, the MINIRAM must be in its off condition (press OFF in case of doubt). Then, press ZERO and wait until the display again indicates "OFF".

The average of 4 consecutive 10-second zero level measurements will then be stored by the MINIRAM as the new ZERO reference value. When operating the MINIRAM in high particle concentration environments (>5 mg/m^3) the zero value update should be performed approximately every 8 hours. At aerosol concentrations below approximately 1 mg/m^3 this update may only be required once a week, or even less frequently. The zero update should be performed either within a clean-air environment (ideally, a clean room or clean bench). Air conditioned offices (without smokers) usually have concentrations below approximately 0.05 mg/m^3 and can thus be used for zeroing purposes. When measurements are performed under essentially clean air conditions, e.g., in the same environment where the zero check was performed, the MINIRAM readings will indicate 0.00 mg/m^3 with small random fluctuations around that value. Positive values (e.g., 0.02) will thus be indicated on the LCD display. Negative values (e.g.,-0.02) are suppressed and are also indicated as 0.00. The digital output, however, does include such negative values and these can be printed out on a digital printer.

<u>High Volume Pump Calibration</u>

High volume air pumps will be calibrated after shipping to the site and again at the end of the sampling, prior to being returned. The calibration of the pumps will be conducted using a 5-plate calibration kit as described in 40 CFR Part 50 Appendix B "Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method)." The calibration procedure is as follows:

1. Assemble the blower/motor and filter holder with the orifice meter plate in place between them.

2. Attach each leg of a water manometer to the two pressure taps on the blower/motor and the filter holder. Label this manometer A.

3. Attach the top loading adapter plate to the filter holder and install the calibration orifice with the appropriate load plate (number 18 hole plate) onto the top loading adapter plates.

4. Connect one leg of a water manometer to the calibrated orifice. Label this manometer B.

5. Turn the motor on.

6. Read the manometer labeled B and convert it to actual flow rate using the curve supplied with the orifice.

7. Read manometer A.

8. Record the actual flow rate and the differential pressure figure that was obtained from manometer A on the data sheet (Figure 2-2).

9. Use the remaining load plates (using the plate with the next fewest number of holes next) until the actual flow rates and differential pressures have been established.

10. Using the readings established with the procedure above, plot a curve which will represent the actual versus indicated flow rates.

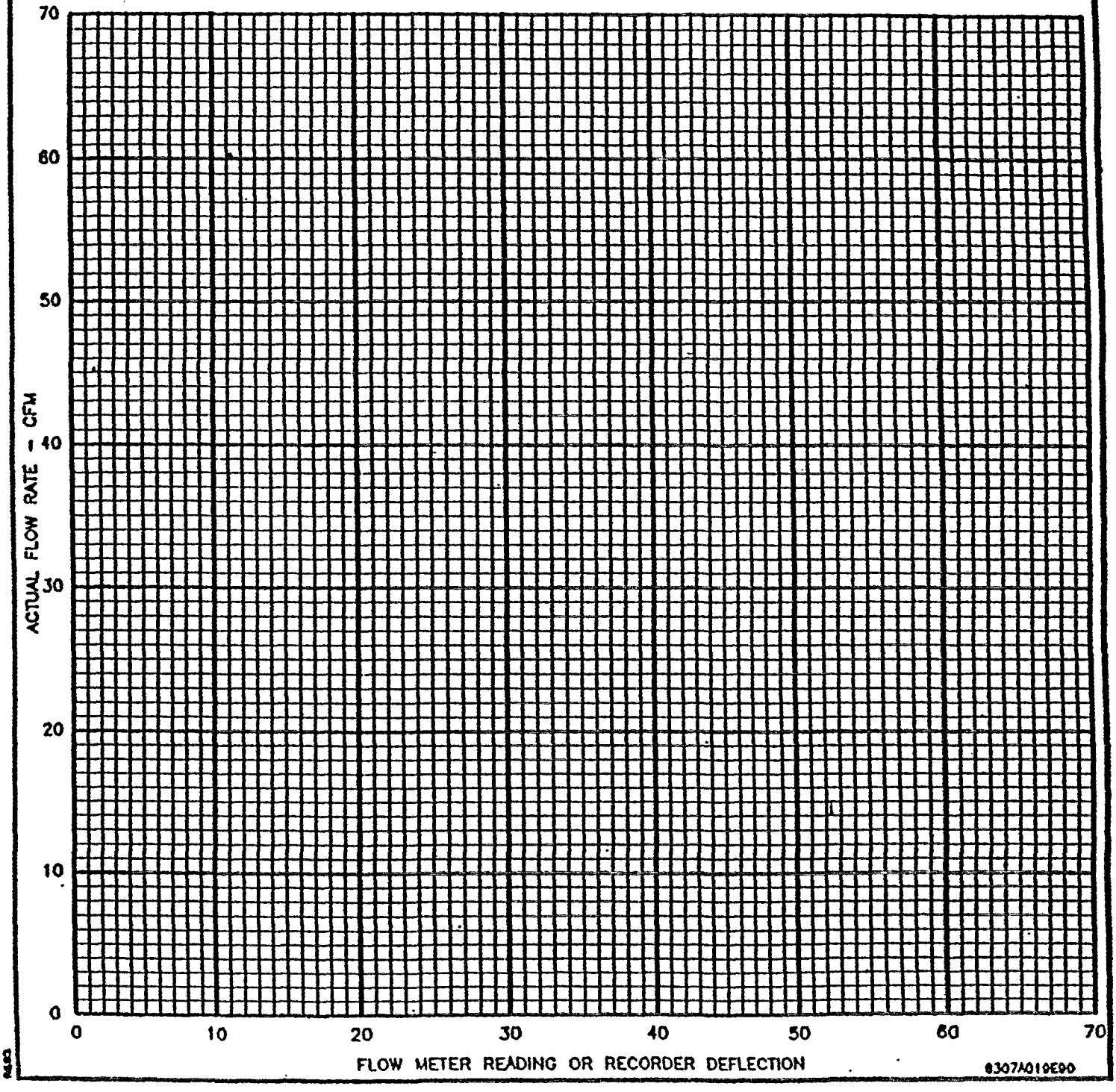
HIGH VOLUME AIR SAMPLER CALIBRATION Unit No.: _____

DATE: BY:

TEMP.: AT. PRESS:

REMARKS:

Plate	Indicated	True "H_2O	Actual cfm
18			
13			
10			
7			
5			



11. This new calibration curve is used as a direct reference to obtain the actual flow rate in the field.

12. To operate, remove calibration equipment; however, leave manometer A in place. This manometer will be used to take flow measurements at the beginning and the end of the sampling period.

PS-1 Sampler Calibration

1. Calibration of the PUF sampler is performed without a foam plug or filter paper in the sampling module. However, the empty glass cartridge must remain in the module to insure a good seal through the module.

2. Install the GMW-40 Calibrator on top of the 4" filter holder.

3. Connect an 8" water manometer to the Calibrator.

4. Open the ball valve fully.

5. Turn the system on by tripping the manual switch on the timer. Allow a few minutes for warm-up.

6. Adjust the voltage control screw to obtain a reading of 70 inches on the dial gage, (Magnehelic Gage).

7. With 70 inches on the dial gage as your first calibration point, record it and the manometer reading on the data sheet (Figure 2-3).

8. Close the ball valve slightly to readjust the dial gage down to 60 inches. Record this figure and manometer reading on the data sheet.

CALIBRATION DATA SHEET

HIGH VOLUME AIR SAMPLER CALIBRATION

Unit No.: _____

Date:

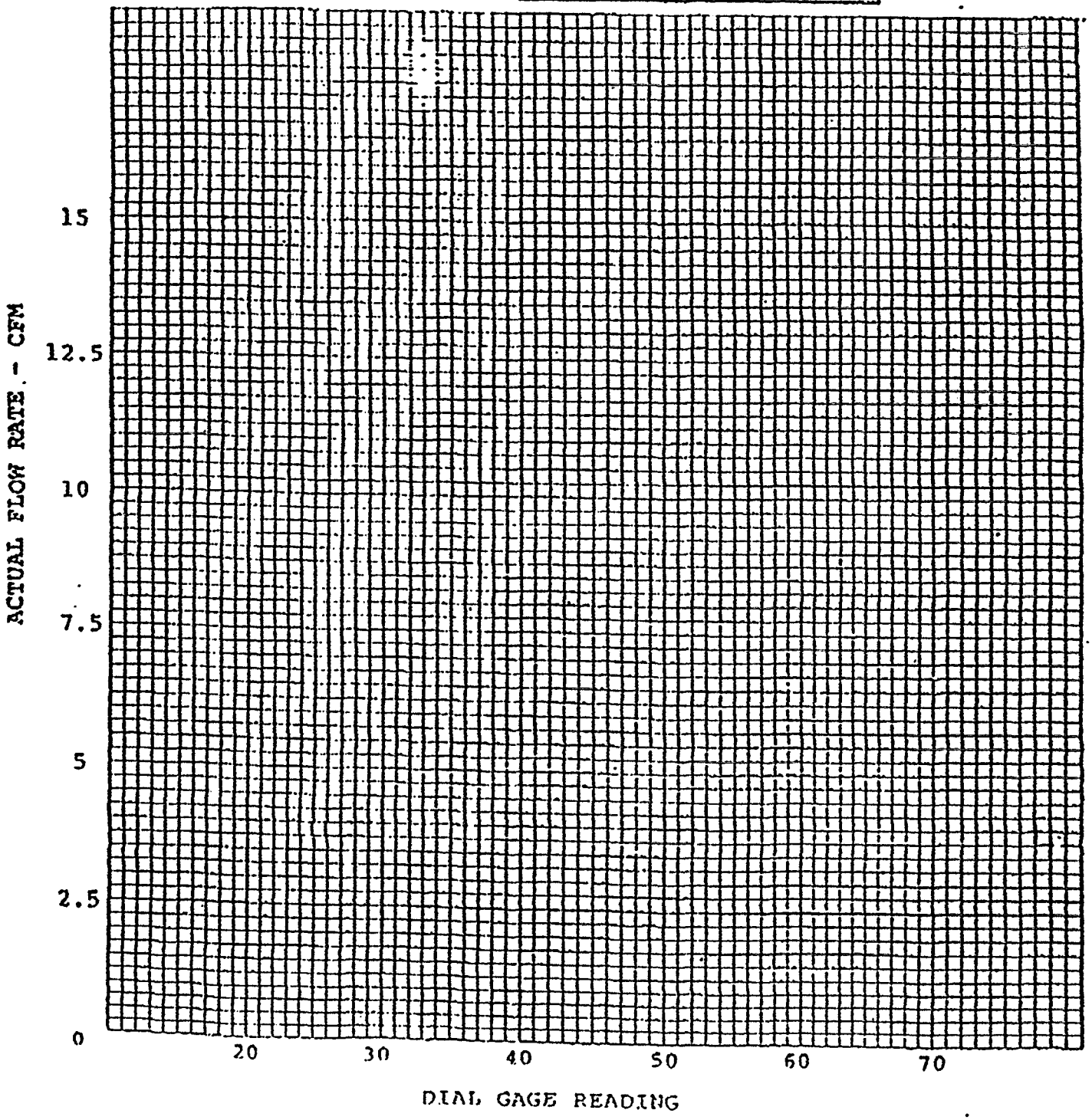
By:

Temp.:

At. Press:

Remarks:

Indicated	True "H_2O	Actual cfm



9. Using the above procedure, adjust the ball valve for readings at 50, 40 and 30 inches and record on the data sheet.

10. Using these two sets of readings, plot a curve on the data sheet. This curve will be used for determining the actual flow rate in the field.

11. Readjust the voltage control fully clockwise to its maximum setting. Open ball valve fully.

2.7.2 Wind Instrument Calibration

The calibration of the wind monitoring instrument will be in accordance with the recommendations of the manufacturer of the equipment selected for this project.

2.7.3 Sample Preservation

Immediately after sampling, Tenex[R] tubes will be sealed in a friction-top tube or can containing a layer of charcoal as described in EPA method TO1. The Tenex[R] tubes will be stored on ice, packaged for shipment to the laboratory for analysis and shipped to the laboratory by next-day delivery.

The 8 x 10 inch glass fiber filters used to collect samples for lead analysis are stable and may be held at ambient conditions in sealed plastic bags until the analysis is desired.

For the samples collected by EPA Methods TO4 and TO13 for PCB and PNAs respectively, the glass fiber filter will be folded and placed inside the glass cartridge on top of the PUF plug. The cartridge will then be wrapped with aluminum foil and placed in a glass jar with a screw-top lid. The samples will be stored on ice, packed for shipment to the laboratory for analysis and shipped to the laboratory by next-day delivery.

2.7.4 Sample Handling

For each sample collected, an entry will be made on the form shown in Figure 2-1. All samples and blanks will be labeled with the sample number, date and the initials of the individual collecting the sample. The samples will be shipped to the laboratory by overnight delivery for analysis of the constituents of concern. Relevant sample information will be entered on a chain-of-custody form (Figure 2-4) at the conclusion of sampling. Shipping and all subsequent off site handling of samples will be documented on the chain-of-custody forms.

2.7.5 Field Blanks

Field blanks will constitute ten percent (10%) of the total number of samples collected. These blanks will be entered on the form shown in Figure 2-1 as a sample. All blanks will be labeled with a sample number, date and the initial of the individual collecting the samples. Field blanks will be entered on the chain-of-custody as a sample so that they are not known as blanks to the laboratory.

2.7.6 Laboratory Quality Assurance/Quality Control

A summary report of the laboratory quality assurance and quality control (QA/QC) measures will be requested from the analytical laboratories. This report will include the results of laboratory blanks, spikes and duplicates. This QA/QC report will be included as part of the sample analytical reports.

Project No.	Project Name:												
Samplers: (Signatures)													
Sample No.	Date	Name or Sample Location	Number of Containers	METHOD									REMARKS Sample Volume (L)-or Elapsed Time (min)
Relinquished by:(Signature)		Date	Time	Received by (Signature)			Relinquished by: (Signature)				Date	Time	Received by: (Signature)
Relinquished by:(Signature)		Date	Time	Received for Laboratory by:(Signature)				Date	Time	Remarks			

EAGLE ENVIRONMENTAL HEALTH, INC.

3 - SAMPLE COLLECTION STRATEGY

Air monitoring will be conducted during activities which could potentially result in air emissions of site constituents during Phase I and Phase II Removal Action activities. Monitoring for volatile organic vapors (real-time and integrated sampling) will occur throughout the duration of the project and will take place during activities that have the potential for air emission of volatile organics. Monitoring for particulates (real-time and integrated sampling), PCBs (integrated sampling only); PNAs (integrated sampling only) and lead (integrated sampling only) will be conducted only during the initial phases of those activities which may produce emissions. Emissions of particulates, PCBs, PNAs and lead to the air are expected to be negligible based on the nature of the work, the compounds' low volatility and low potential to become airborne, and previous air monitoring for these compounds at the site. Sampling will occur in the Pond Area and/or the Process Area depending upon the location of Removal Action activities that may produce the potential for emission. Action levels are summarized in Tables 3-1 and 3-2. Derivation of the air action levels in Table 3-2 is provided in Appendix E. The air monitoring strategy is described in detail below.

3.1 Real-time Sampling

Real-time sampling for volatile organic vapors and particulates will be conducted using one upwind instrument and one downwind instrument positioned at the Process Area and Pond Area fenceline. Real-time instrument locations may be changed during the day to accommodate changing wind direction. Draeger Tube field detection kits specific to benzene and/or toluene will also be available to check for the presence of these specific compounds. The Draeger tubes will be used on an as requested basis in response to increased odors or residential complaints.

Table 3-1

Summary of Response Actions
to Exceedance of Action Levels

Sample Type	Sample Frequency (a)	Parameter	Action Level	Response
OVM	continuous	total volatile organic compounds	0-3 ppm above background	green light - proceed with work
			>3 ppm, <5 ppm above background for greater than 5 minutes(b)	yellow light - modify or slow work
			>5 ppm for greater than 5 minutes(b)	red light - stop work and modify procedures
MINIRAM	continuous	total dust	>3.6 mg/m^3 for greater than 5 minutes(b)	slow work and modify procedures

(a) Sampling will be conducted only in the areas where project activities are under way with the potential for the type of emissions shown. Sampling location will be at the fenceline.

(b) Measured as an average over five minutes with one minute readings taken.

TABLE 3-2

ACTION LEVELS FOR SPECIFIC CHEMICALS IN AIR
PHASE I AND PHASE II REMOVAL ACTION

Combustion, Inc. Site
Denham Springs, Louisiana

Parameters	Method Detection Limits (a) ug/m^3	Action Levels [(b)(c)(d)(e)(f)] ug/m^3
Benzene (b)	4	84
Chlorobenzene (f)	67	200
Chloroethane (f)	3,333	10,000
Chloroform (b)	2	30
1,1-Dichloroethane (f)	1667	5000
1,2-Dichloroethane (b)	1	27
1,2-Dichloroethene ---	50	Monitor Only
1,4-Dichlorobenzene(f)	233	700
Ethyl benzene (f)	333	1000
Styrene (b)	61	1220
Tetrachloroethene (b)	67	1340
Toluene (f)	667	2000
Trichloroethene (b)	21	420
Xylenes (f)	100	300
PCBs (h)	0.5	1
PNAs (b)(g)	0.2	4
Lead (g)	0.5	1.5

TABLE 3-2 (cont'd.)

ACTION LEVELS FOR SPECIFIC CHEMICALS IN AIR
PHASE I AND PHASE II REMOVAL ACTION

Combustion, Inc. Site
Denham Springs, Louisiana

Notes:

(a) These are the target detection limits but may be modified depending on matrix interference and other laboratory factors.

(b) Action levels derived using a 1×10^{-5} cancer risk factor for carcinogenic compounds.

(c) Action levels reflect exposure durations adjusted for a maximum seasonal wind direction of 50% (e.g., no one receptor is downwind of the site more than 50% of the time over a two-year period). Therefore, exposure duration equals (project time) X 0.5. Reference Wind Rose charts found in Appendix E.

(d) Actions levels equate to the running average of the downwind data results and not instantaneous or maximum daily readings.

(e) Action levels must be corrected for background levels.

(f) Action levels based on two years of field construction activity; derived using non-carcinogenic health effects subchronic reference concentrations (RFC) and a Hazard Index of one.

(g) Equivalents to benzo(a)pyrene. See Appendix E for equivalent factors for specific PNAs.

(h) National Institute for Occupational Safety and Health (NIOSH) proposed standard and referenced by EPA Region VI.

3.1.1 Volatile Organic Compound Action Levels

The action levels for photoionization detector readings are shown in Table 3-1. If the action level is exceeded at the downwind monitoring location, the work will immediately be slowed or halted until the source is identified and controlled. The PID will also be taken off site to determine if there are air emissions outside the fence line and in the adjacent neighborhood. If emissions are above the fence line action level in any off site areas, on-site work will be immediately suspended.

3.1.2 Particulate Action Levels

The action levels for the MINIRAM readings are also shown in Table 3-1. If the action level is exceeded at the downwind monitoring point, the work will immediately be slowed or halted until the source is identified and controlled. The MINIRAM will also be taken off site to determine the air emissions outside the fence line and in the adjacent neighborhood. If emissions are above the fence line action level in any off site areas, on-site work will be immediately suspended.

3.2 Integrated Sampling

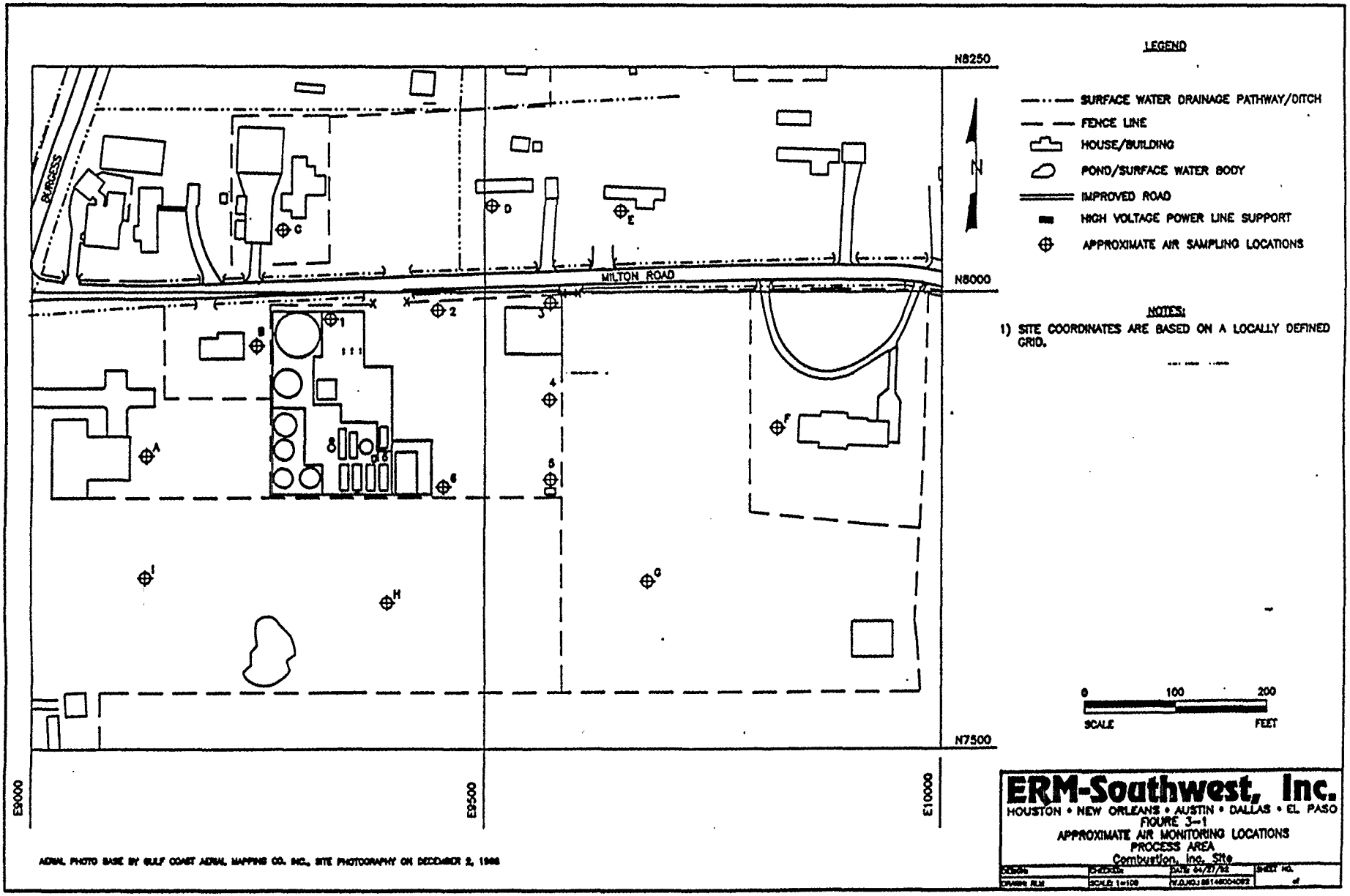
3.2.1 Sampling Approach

Potential integrated sample locations have been tentatively selected as shown in Figures 3-1 and 3-2. These locations may vary somewhat depending on the work in progress and the wind direction. The off site locations (indicated by letters on the figures) will be used only if the land owners grant permission for the sampling to be performed, since these locations are private property.

At the start of each day of activities requiring monitoring, three of the mapped locations will be selected based on the prevailing wind direction for sampling at the area to be monitored. One sampling location will be selected upwind of the work area at the fence line. Two sampling locations will be selected at the nearest downwind locations (assuming property access is permitted). Off site sample locations will generally be at the nearest downwind residence; where the distance to the nearest downwind residences is great; however, the locations will be closer to the fence line as shown in Figure 3-1 and 3-2.

An additional downwind sample location will be at the fence line. The selection of sampling locations will be made each day in consultation with the on-site DEQ or EPA representative, if available. Volatile organics, lead, PCBs and/or PNAs will be sampled depending upon the area of activity, project timing and the nature of the potential release. All samples will be sent to the laboratory, but only the two off site downwind samples will be analyzed initially. The upwind sample and downwind fence line sample will be archived (for a maximum of 7 days after receipt of downwind sample results) and may be analyzed if warranted by the results of the initial sample or at the request of the DEQ or EPA representatives. All samples will be collected for the duration of the work day. Sampling station inlets will be located 3 to 4 feet above grade.

Samples for volatile organics will be collected every working day that material handling occurs. Sampling for lead will only take place on days when a dust hazard could be created (i.e., digging up underground storage tanks). Sampling for PNAs and PCBs will only take place in the Pond Area at the time pond oil removal is initiated. Six consecutive days of sampling will alternate between PNA and PCB monitoring. This strategy has been selected because both methods utilize the same sampling equipment and cannot be collected simultaneously. After the six days of sampling have been completed, the analysis results will be compared to the action levels to determine if additional sampling for PCBs and PNAs is appropriate.



AERIAL PHOTO BASE BY GULF COAST AERIAL MAPPING CO. INC., SITE PHOTOGRAPHY ON DECEMBER 2, 1988

ERM-Southwest, Inc.

HOUSTON • NEW ORLEANS • AUSTIN • DALLAS • EL PASO

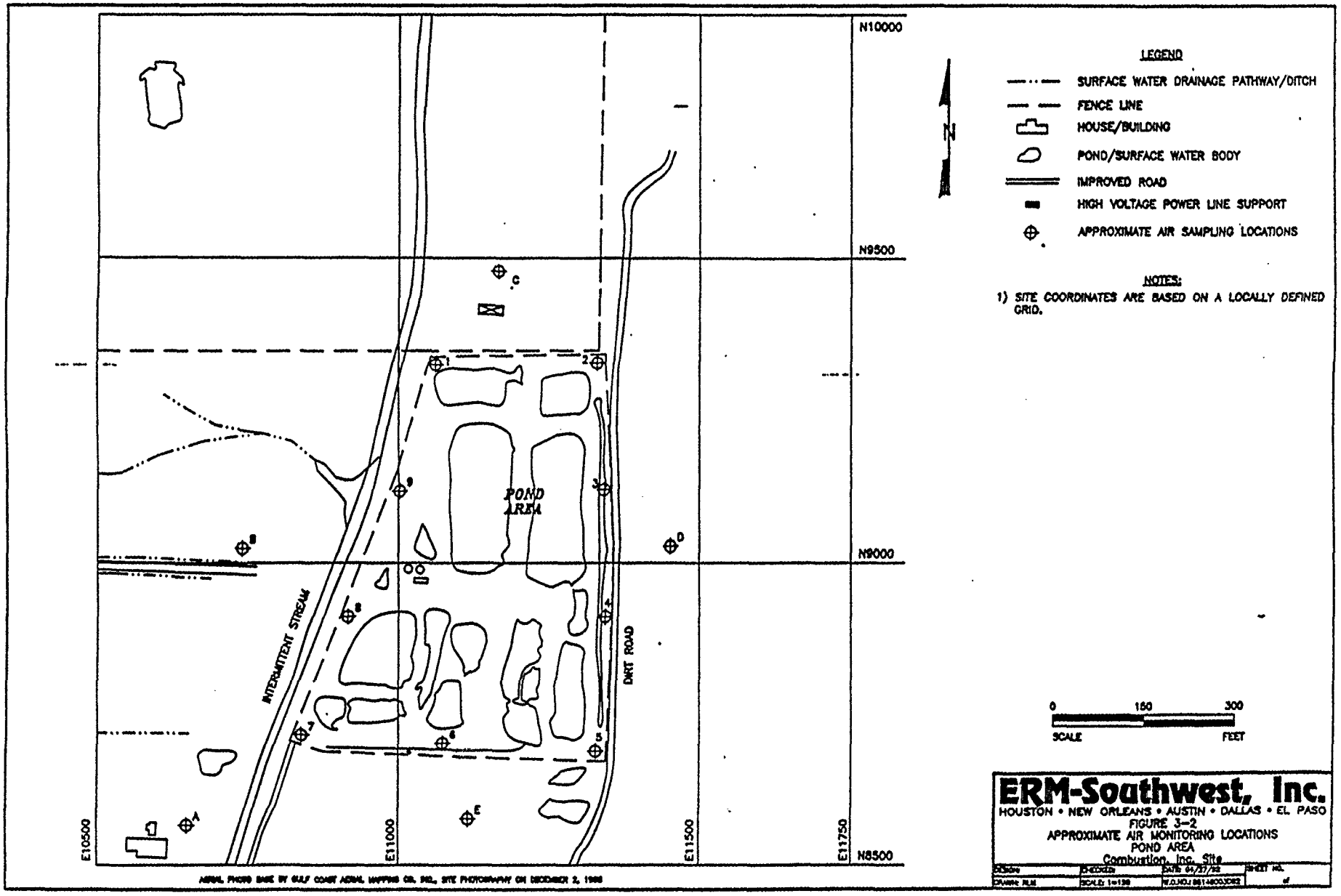
FIGURE 3-1

APPROXIMATE AIR MONITORING LOCATIONS

PROCESS AREA

Combustion, Inc. Site

DESIGN	PROJECT	DATE 04/27/92	SHEET NO.
DRAWN RLM	SCALE 1=100	W.O.NO.8814800-0092	of



AERIAL PHOTO BASE BY GULF COAST AERIAL MAPPING CO., INC., SITE PHOTOGRAPHY ON DECEMBER 2, 1988

3.2.2 Action Levels

The Tenex[R] samples which will be collected for analysis for specific organic compounds, the glass fiber filters which will be analyzed for lead, and the PUF cartridges to be analyzed for PCBs or PNAs require laboratory analysis. Therefore, their results will not be immediately known on-site. As data is received from the laboratory on these constituents, it will be analyzed and reported.

Analyses and response to the reported data will be as follows:

1. All analyses reported below the minimum detection limits shown in Table 3-2 (after correction for background) will simply be logged and reported. Analyses below the detection limits indicates cleanup may proceed unmodified. This is a green light condition.

2. Single analyses reported above the detection limit but below the action level (after correction for background) shall be reported to the regulatory agency within two days of receipt of the validated data. Onsite activities performed on the day of the sampling shall be reviewed to determine the potential source(s) of emissions and corrective measures will be considered. This is a green light condition with caution.

3. Single analyses reported above the action level but with the running average below the action level (after correction for background) shall be reported to the agency within two days of receipt of the validated data. All waste handling activities shall be immediately reviewed and the work shall be slowed or suspended until corrective measures are implemented. This is a yellow light condition.

4. If the running average of the downwind data (corrected for background) exceeds 0.9 times the action level, all work shall be suspended until corrective measures are taken and the regulatory agencies authorize restart of the work. This is a red light condition.

4 - SAMPLING RESULTS

Real time monitoring data will be recorded in a bound log book that will be kept on-site and will be available for DEQ/EPA review. Laboratory analyses will be provided to DEQ/EPA within ten days of receipt and validation except as discussed in Section 3.2.2. Copies of the laboratory reports will also be kept on-site and will be available for DEQ/EPA review.

APPENDIX A

EPA METHOD TO1

APPENDIX A
EPA METHOD TO1

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING TENAX® ADSORPTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Scope

1.1 The document describes a generalized protocol for collection and determination of certain volatile organic compounds which can be captured on Tenax® GC (poly(2,6-Diphenyl phenylene oxide)) and determined by thermal desorption GC/MS techniques. Specific approaches using these techniques are described in the literature (1-3).

1.2 This protocol is designed to allow some flexibility in order to accommodate procedures currently in use. However, such flexibility also results in placement of considerable responsibility with the user to document that such procedures give acceptable results (i.e. documentation of method performance within each laboratory situation is required). Types of documentation required are described elsewhere in this method.

1.3 Compounds which can be determined by this method are nonpolar organics having boiling points in the range of approximately 80° - 200°C. However, not all compounds falling into this category can be determined. Table 1 gives a listing of compounds for which the method has been used. Other compounds may yield satisfactory results but validation by the individual user is required.

2. Applicable Documents

2.1 ASTM Standards:

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis.

E355 Recommended Practice for Gas Chromatography Terms and Relationships.

2.3 Other documents:

Existing procedures (1-3).
U.S. EPA Technical Assistance Document (4).

3. Summary of Protocol

3.1 Ambient air is drawn through a cartridge containing ~1-2 grams of Tenax and certain volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed.

3.2 For analysis the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the volatile organic compounds from the cartridge onto a cold trap and subsequently onto the front of the GC column which is held at low temperature (e.g. - 70°C). The GC column temperature is then increased (temperature programmed) and the components eluting from the column are identified and quantified by mass spectrometry. Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics. Less sophistacated detectors (e.g. electron capture or flame ionization) may be used for certain applications but their suitability for a given application must be verified by the user.

3.3 Due to the complexity of ambient air samples only high resolution (i.e. capillary) GC techniques are considered to be acceptable in this protocol.

4. Significance

4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage facilities, etc. Many of these compounds are toxic; hence knowledge of the levels of

such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Conventional air monitoring methods (e.g. for workspace monitoring) have relied on carbon adsorption approaches with subsequent solvent desorption. Such techniques allow subsequent injection of only a small portion, typically 1-5% of the sample onto the GC system. However, typical ambient air concentrations of these compounds require a more sensitive approach. The thermal desorption process, wherein the entire sample is introduced into the analytical (GC/MS) system fulfills this need for enhanced sensitivity.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356(6). All abbreviations and symbols are defined with this document at the point of use.

6. INTERFERENCES

6.1 Only compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere in the method. The most commonly encountered interferences are structural isomers.

6.2 Contamination of the Tenax cartridge with the compound(s) of interest is a commonly encountered problem in the method. The user must be extremely careful in the preparation, storage, and handling of the cartridges throughout the entire sampling and analysis process to minimize this problem.

7. Apparatus

7.1 Gas Chromatograph/Mass Spectrometry system - should be capable of subambient temperature programming. Unit mass resolution or better up to 800 amu. Capable of scanning 30-440 amu region every 0.5-1 second. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2 Thermal Desorption Unit - Designed to accommodate Tenax cartridges in use. See Figure 2a or b.

7.3 Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the Tenax cartridge. (See Figure 3a or b.)

7.4 Vacuum oven - connected to water aspirator vacuum supply.

7.5 Stopwatch

7.6 Pyrex disks - for drying Tenax.

7.7 Glass jar - Capped with Teflon-lined screw cap. For storage of purified Tenax.

7.8 Powder funnel - for delivery of Tenax into cartridges.

7.9 Culture tubes - to hold individual glass Tenax cartridges.

7.10 Friction top can (paint can) - to hold clean Tenax cartridges.

7.11 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired. (optional)

7.12 Thermometer - to record ambient temperature.

7.13 Barometer (optional).

7.14 Dilution bottle - Two-liter with septum cap for standards preparation.

7.15 Teflon stirbar - 1 inch long.

7.16 Gas-tight glass syringes with stainless steel needles - 10-500 µl for standard injection onto GC/MS system.

7.17 Liquid microliter syringes - 5.50 µL for injecting neat liquid standards into dilution bottle.

7.18 Oven - 60 $\pm$ 5°C for equilibrating dilution flasks.

7.19 Magnetic stirrer.

7.20 Heating mantel.

7.21 Variac

7.22 Soxhlet extraction apparatus and glass thimbles - for purifying Tenax.

7.23 Infrared lamp - for drying Tenax.

7.24 GC column - SE-30 or alternative coating, glass capillary or fused silica.

7.25 Psychrometer - to determine ambient relative humidity. (optional).

8. Reagents and Materials

8.1 Empty Tenax cartridges - glass or stainless steel (See Figure 1a or b).
8.2 Tenax 60/80 mesh (2,6-diphenylphenylene oxide polymer).
8.3 Glasswool - silanized.
8.4 Acetone - Pesticide quality or equivalent.
8.5 Methanol - Pesticide quality, or equivalent.
8.6 Pentane - Pesticide quality or equivalent.
8.7 Helium - Ultra pure, compressed gas. (99.9999%)
8.8 Nitrogen - Ultra pure, compressed gas. (99.9999%)
8.9 Liquid nitrogen.
8.10 Polyester gloves - for handling glass Tenax cartridges.
8.11 Glass Fiber Filter - one inch diameter, to fit in filter holder. (optional)
8.12 Perfluorotributylamine (FC-43).
8.13 Chemical Standards - Neat compounds of interest. Highest purity available.
8.14 Granular activated charcoal - for preventing contamination of Tenax cartridges during storage.

9. Cartridge Construction and Preparation

9.1 Cartridge Design

9.1.1 Several cartridge designs have been reported in the literature (1-3). The most common (1) is shown in Figure 1a. This design minimizes contact of the sample with metal surfaces, which can lead to decomposition in certain cases. However, a disadvantage of this design is the need to rigorously avoid contamination of the outside portion of the cartridge since the entire surface is subjected to the purge gas stream during the desorption porcess.

hours in a hood. Care must be exercised to avoid over heating of the Tenax by the infrared lamp. The Tenax is then placed in a vacuum oven (evacuated using a water aspirator) without heating for one hour. An inert gas (helium or nitrogen) purge of 2-3 ml/minute is used to aid in the removal of solvent vapors. The oven temperature is then increased to 110°C, maintaining inert gas flow and held for one hour. The oven temperature control is then shut off and the oven is allowed to cool to room temperature. Prior to opening the oven, the oven is slightly pressurized with nitrogen to prevent contamination with ambient air. The Tenax is removed from the oven and sieved through a 40/60 mesh sieve (acetone rinsed and oven dried) into a clean glass vessel. If the Tenax is not to be used immediately for cartridge preparation it should be stored in a clean glass jar having a Teflon-lined screw cap and placed in a desiccator.

9.3 Cartridge Preparation and Pretreatment

9.3.1 All cartridge materials are pre-cleaned as described in Section 9.2.2. If the glass cartridge design shown in Figure 1a is employed all handling should be conducted wearing polyester gloves.

9.3.2 The cartridge is packed by placing a 0.5-1cm glass-wool plug in the base of the cartridge and then filling the cartridge to within approximately 1 cm of the top. A 0.5-1cm glasswool plug is placed in the top of the cartridge.

9.3.3 The cartridges are then thermally conditioned by heating for four hours at 270°C under an inert gas (helium) purge (100 - 200 ml/min).

9.3.4 After the four hour heating period the cartridges are allowed to cool. Cartridges of the type shown in Figure 1a are immediately placed (without cooling) in clean culture tubes having Teflon-lined screw caps with a glasswool cushion at both the top and the bottom. Each tube should be shaken to ensure that the cartridge is held firmly in place. Cartridges of the type shown in Figure 1b are allowed to cool to room temperature under inert gas purge and are then closed with stainless steel plugs.

9.3.5 The cartridges are labeled and placed in a tightly sealed metal can (e.g. paint can or similar friction top container). For cartridges of the type shown in Figure 1a the culture tube, not the cartridge, is labeled.

9.3.6 Cartridges should be used for sampling within 2 weeks after preparation and analyzed within two weeks after sampling. If possible the cartridges should be stored at -20°C in a clean freezer (i.e. no solvent extracts or other sources of volatile organics contained in the freezer).

10. Sampling

10.1 Flow rate and Total Volume Selection

10.1.1 Each compound has a characteristic retention volume (liters of air per gram of adsorbent) which must not be exceeded. Since the retention volume is a function of temperature, and possibly other sampling variables, one must include an adequate margin of safety to ensure good collection efficiency. Some considerations and guidance in this regard are provided in a recent report (5). Approximate breakthrough volumes at 38°C (100°F) in liters/gram of Tenax are provided in Table 1. These retention volume data are supplied only as rough guidance and are subject to considerable variability, depending on cartridge design as well as sampling parameters and atmospheric conditions.

10.1.2 To calculate the maximum total volume of air which can be sampled use the following equation:

$$V_{MAX} = \frac{V_b \times W}{1.5}$$

where

V_{MAX} is the calculated maximum total volume in liters.

V_b is the breakthrough volume for the least retained compound of interest (Table 1) in liters per gram of Tenax.

W is the weight of Tenax in the cartridge, in grams.

1.5 is a dimensionless safety factor to allow for variability in atmospheric conditions. This factor is appropriate for temperatures in the range of 25-30°C. If higher temperatures are encountered the factor should be increased (i.e. maximum total volume decreased).

10.1.3 To calculate maximum flow rate use the following equation:

$$Q_{MAX} = \frac{V_{MAX}}{t} \times 1000$$

where

Q_{MAX} is the calculated maximum flow rate in milliliters per minute.

t is the desired sampling time in minutes. Times greater than 24 hours (1440 minutes) generally are unsuitable because the flow rate required is too low to be accurately maintained.

10.1.4 The maximum flow rate Q_{MAX} should yield a linear flow velocity of 50-500 cm/minute. Calculate the linear velocity corresponding to the maximum flow rate using the following equation:

$$B = \frac{Q_{MAX}}{\pi r^2}$$

where

B is the calculated linear flow velocity in centimeters per minute.

r is the internal radius of the cartridge in centimeters.

If B is greater than 500 centimeters per minute either the total sample volume (V_{MAX}) should be reduced or the sample flow rate (Q_{MAX}) should be reduced by increasing the collection time. If B is less than 50 centimeters per minute the sampling rate (Q_{MAX}) should be increased by reducing the sampling time. The total sample value (V_{MAX}) cannot be increased due to component breakthrough.

10.1.4 The flow rate calculated as described above defines the maximum flow rate allowed. In general, one should collect additional samples in parallel, for the same time period but at lower flow rates. This practice yields a measure of quality control and is further discussed in the literature (5). In general, flow rates 2 to 4 fold lower than the maximum flow rate should be employed for the parallel samples. In all cases a constant flow rate should be achieved for each cartridge since accurate integration of the analyte concentration requires that the flow be constant over the sampling period.

10.2 Sample Collection

10.2.1 Collection of an accurately known volume of air is critical to the accuracy of the results. For this reason the use of mass flow controllers, rather than conventional needle valves or orifices is highly recommended, especially at low flow velocities (e.g. less than 100 milliliters/minute). Figure 3a illustrates a sampling system utilizing mass flow controllers. This system readily allows for collection of parallel samples. Figures 3b shows a commercially available system based on needle valve flow controllers.

10.2.2 Prior to sample collection insure that the sampling flow rate has been calibrated over a range including the rate to be used for sampling, with a "dummy" Tenax cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter. The flow calibration device is connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D3686 describes an appropriate calibration scheme, not requiring a sealed flow system downstream of the pump.

10.2.3 The flow rate should be checked before and after each sample collection. If the sampling interval exceeds four hours the flow rate should be checked at an intermediate point during sampling as well. In general, a rotameter should be included, as showed in Figure 3b, to allow observation of the sampling flow rate without disrupting the sampling process.

10.2.4 To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process. If glass cartridges (Figure 1a) are employed they must be handled only with polyester gloves and should not contact any other surfaces.

10.2.5 A particulate filter and holder are placed on the inlet to the cartridges and the exit end of the cartridge is connected to the sampling apparatus. In many sampling situations the use of a filter is not necessary if only the total concentration of a component is desired. Glass cartridges of the type shown in Figure 1a are connected using teflon ferrules and Swagelok (stainless steel or teflon) fittings. Start the pump and record the following parameters on an appropriate data sheet (Figure 4): data, sampling location, time, ambient temperature, barometric

pressure, relative humidity, dry gas meter reading (if applicable) flow rate, rotameter reading (if applicable), cartridge number and dry gas meter serial number.

10.2.6 Allow the sampler to operate for the desired time, periodically recording the variables listed above. Check flow rate at the midpoint of the sampling interval if longer than four hours.
At the end of the sampling period record the parameters listed in 10.2.5 and check the flow rate and record the value. If the flows at the beginning and end of the sampling period differ by more than 10% the cartridge should be marked as suspect.

10.2.7 Remove the cartridges (one at a time) and place in the original container (use gloves for glass cartridges). Seal the cartridges or culture tubes in the friction-top can containing a layer of charcoal and package for immediate shipment to the laboratory for analysis. Store cartridges at reduced temperature (e.g. - 20°C) before analysis if possible to maximize storage stability.

10.2.8 Calculate and record the average sample rate for each cartridge according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where

Q_A = Average flow rate in ml/minute.

$Q_1, Q_2, \ldots Q_N$ = Flow rates determined at beginning, end, and immediate points during sampling.

N = Number of points averaged.

10.2.9 Calculate and record the total volumetric flow for each cartridge using the following equation:

$$V_m = \frac{T \times Q_A}$$

where

V_m = Total volume sampled in liters at measured temperature and pressure.

T_2 = Stop time.

T_1 = Start time.

T = Sampling time = $T_2 - T_1$, minutes

10.2.10 The total volume (V_s) at standard conditions, 25°C and 760 mmHg, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where

P_A = Average barometric pressure, mmHg

t_A = Average ambient temperature, °C.

11. GC/MS Analysis

11.1 Instrument Set-up

11.1.1 Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 14 discusses specific performance criteria which should be met.

11.1.2 A block diagram of the typical GC/MS system required for analysis of Tenax cartridges is depicted in Figure 5. The operation of such devices is described in 11.2.4. The thermal desorption module must be designed to accommodate the particular cartridge configuration. Exposure of the sample to metal surfaces should be minimized and only stainless steel, or nickel metal surfaces should be employed.

The volume of tubing and fittings leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

11.1.3 The GC column inlet should be capable of being cooled to -70°C and subsequently increased rapidly to approximately 30°C. This can be most readily accomplished using a GC equipped with subambient cooling capability (liquid nitrogen) although other approaches such as manually cooling the inlet of the column in liquid nitrogen may be acceptable.

11.1.4 The specific GC column and temperature program employed will be dependent on the specific compounds of interest. Appropriate conditions are described in the literature (1-3). In general a nonpolar stationary phase (e.g. SE-30, OV-1) temperature programmed from 30°C to 200°C at 8°/minute will be suitable. Fused silica bonded phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GC/MS transfer line.

11.1.5 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.

11.1.6 Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 5. Helium purge flows (through the cartridge) and carrier flow are set at approximately 10 ml/minute and 1-2 ml/minute respectively. If applicable, the injector sweep flow is set at 2-4 ml/minute.

11.1.7 Once the column and other system components are assembled and the various flows established the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

11.1.8 The MS and data system are set according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately 5×10^4 should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.2. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.2 Instrument Calibration

11.2.1 Tuning and mass standarization of the MS system is performed according to manufacturer's instructions and relevant information from the user prepared SOP. Perfluorotributylamine should generally be employed for this purpose. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g. lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria.

However, these alternate values must be repeatable on a day-to-day basis.

11.2.2 After the mass standarization and tuning process has been completed and the appropriate values entered into the data system the user should then calibrate the entire system by introducing known quantities of the standard components of interest into the system. Three alternate procedures may be employed for the calibration process including 1) direct syringe injection of dilute vapor phase standards, prepared in a dilution bottle, onto the GC column, 2) Injection of dilute vapor phase standards into a carrier gas stream directed through the Tenax cartridge, and 3) introduction of permeation or diffusion tube standards onto a Tenax cartridge. The standards preparation procedures for each of these approaches are described in Section 13. The following paragraphs describe the instrument calibration process for each of these approaches.

11.2.3 If the instrument is to be calibrated by direct injection of a gaseous standard, a standard is prepared in a dilution bottle as described in Section 13.1. The GC column is cooled to -70°C (or, alternately, a portion of the column inlet is manually cooled with liquid nitrogen). The MS and data system is set up for acquisition as described in the relevant user SOP. The ionization filament should be turned off during the initial 2-3 minutes of the run to allow oxygen and other highly volatile components to elute. An appropriate volume (less than 1 ml) of the gaseous standard is injected onto the GC system using an accurately calibrated gas tight syringe.

The system clock is started and the column is maintained at -70°C (or liquid nitrogen inlet cooling) for 2 minutes. The column temperature is rapidly increased to the desired initial temperature (e.g. 30°C). The temperature program is started at a consistent time (e.g. four minutes) after injection. Simultaneously the ionization filament is turned on and data acquisition is initiated. After the last component of interest has eluted acquisiton is terminated and the data is processed as described in Section 11.2.5. The standard injection process is repeated using different standard volumes as desired.

11.2.4 If the system is to be calibrated by analysis of spiked Tenax cartridges a set of cartridges is prepared as described in Sections 13.2 or 13.3. Prior to analysis the cartridges are stored as described in Section 9.3. If glass cartridges (Figure 1a) are employed care must be taken to avoid direct contact, as described earlier. The GC column is cooled to -70°C, the collection loop is immersed in liquid nitrogen and the desorption module is maintained at 250°C. The inlet valve is placed in the desorb mode and the standard cartridge is placed in the desorption module, making certain that no leakage of purge gas occurs. The cartridge is purged for 10 minutes and then the inlet valve is placed in the inject mode and the liquid nitrogen source removed from the collection trap. The GC column is maintained at -70°C for two minutes and subsequent steps are as described in 11.2.3. After the process is complete the cartridge is removed from the desorption module and stored for subsequent use as described in Section 9.3.

11.2.5 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 14. If these criteria are not achieved the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

11.3 Sample Analysis

11.3.1 The sample analysis process is identical to that described in Section 11.2.4 for the analysis of standard Tenax cartridges.

11.3.2 Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reverse-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine. As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards is used to calculate a response factor for each component of interest. Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion). In general quantities of component greater than 1000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 In practice the daily routine may not always allow analysis of three such calibration standards. In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. One standard concentration, near the midpoint of the analytical range of interest, should be chosen for injection every day to determine day-to-day response reproducibility.

12.1.3 If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g. quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area

X = quantity of component, nanograms

A,B, and C are coefficients in the equation

12.2 Analyte Concentrations

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX_A$$

where

Y_A is the area of the analyte characteristic ion for the sample cartridge.

X_A is the calculated quantity of analyte on the sample cartridge, in nanograms.

A,B, and C are the coefficients calculated from the calibration curve described in Section 12.1.3.

12.2.2 If instrumental response is essentially linear over the concentration range of interest a linear equation (C=0 in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_S}$$

where

C_A is the calculated concentration of analyte in nanograms per liter.

V_S and X_A are as previously defined in Section 10.2.10 and 12.2.1, respectively.

13. Standard Preparation

13.1 Direct Injection

13.1.1 This process involves preparation of a dilution bottle containing the desired concentrations of compounds of interest for direct injection onto the GC/MS system.

13.1.2 Fifteen three-millimeter diameter glass beads and a one-inch Teflon stirbar are placed in a clean two-liter glass septum capped bottle and the exact volume is determined by weighing the bottle before and after filling with deionized water. The bottle is then rinsed with acetone and dried at 200°C.

13.1.3 The amount of each standard to be injected into the vessel is calculated from the desired injection quantity and volume using the following equation:

$$W_T = \frac{W_I}{V_I} \times V_B$$

where

W_T is the total quantity of analyte to be injected into the bottle in milligrams

W_I is the desired weight of analyte to be injected onto the GC/MS system or spiked cartridge in nanograms

V_I is the desired GC/MS or cartridge injection volume (should not exceed 500) in microliters.

V_B is total volume of dilution bottle determined in 13.1.1, in liters.

13.1.4 The volume of the neat standard to be injected into the dilution bottle is determined using the following equation:

$$V_T = \frac{W_T}{d}$$

where

V_T is the total volume of neat liquid to be injected in microliters.

d is the density of the neat standard in grams per milliliter.

13.1.6 The bottle is placed in a 60°C oven for at least 30 minutes prior to removal of a vapor phase standard.

13.1.7 To withdraw a standard for GC/MS injection the bottle is removed from the oven and stirred for 10-15 seconds. A suitable gas-tight microber syring warmed to 60°C, is inserted through the septum cap and pumped three times slowly. The appropriate volume of sample (approximately 25% larger than the desired injection volume) is drawn into the syringe and the volume is adjusted to the exact value desired and then immediately injected over a 5-10 seconds period onto the GC/MS system as described in Section 11.2.3.

13.2 Preparation of Spiked Cartridges by Vapor Phase Injection

13.2.1 This process involves preparation of a dilution bottle containing the desired concentrations of the compound(s) of interest as described in 13.1 and injecting the desired volume of vapor into a flowing inert gas stream directed through a clean Tenax cartridge.

13.2.2 A helium purge system is assembled wherein the helium flow 20-30 mL/minute is passed through a stainless steel Tee fitted with a septum injector. The clean Tenax cartridge is connected downstream of the tee using appropriate Swagelok fittings. Once the cartridge is placed in the flowing gas stream the appropriate volume vapor standard, in the dilution bottle, is injected through the septum as described in 13.1.6. The syringe is flushed several times by alternately filling the syringe with carrier gas and displacing the contents into the flow stream, without removing the syringe from the septum. Carrier flow is maintain through the cartridge for approximately 5 minutes after injection.

13.3 Preparation of Spiked Traps Using Permeation or Diffusion tubes

13.3.1 A flowing stream of inert gas containing known amounts of each compound of interest is generated according to ASTM Method D3609(6). Note that a method of accuracy maintaining temperature within ± 0.1°C is required and the system generally must be equilibrated for at least 48 hours before use.

13.3.2 An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean Tenax cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed they must be calibrated for the carrier gas used in Section 13.3.1 (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.

13.3.3 The spiked cartridges are then stored or immediately analyzed as in Section 11.2.4.

14. Performance Criteria and Quality Assurance

This section summarizes quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate section describing the particular activity (e.g. parallel sampling).

14.1 Standard Operating Procedures (SOPs)

14.1.1 Each user should generate SOPs describing the following activities as they are performed in their laboratory:

1) assembly, calibration, and operation of the sampling system,
2) preparation, handling and storage of Tenax cartridges,
3) assembly and operation of GC/MS system including the thermal desorption apparatus and data system, and
4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by the laboratory personnel conducting the work.

14.2 Tenax Cartridge Preparation

14.2.1 Each batch of Tenax cartridges prepared (as described in Section 9) should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may chose to use GC/FID due to logistical and cost considerations.

14.2.2 Analysis by GC/FID is accomplished as described for GC/MS (Section 11) except for use of FID detection.

14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

14.3 Sample Collection

14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates as described in Section 10.1. If agreement between parallel samples is not generally within $\pm$ 25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set

of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

14.4 GC/MS Analysis

14.4.1 Performance criteria for MS tuning and mass calibration have been discussed in Section 11.2 and Table 2. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

14.4.2 Chromatographic efficiency should be evaluated using spiked Tenax cartridges since this practice tests the entire system. In general a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level as described in Section 13.2 or 13.3. The cartridge is then analyzed by GC/MS as

described in Section 11.4. The perfluorotoluene (or other reference compound) peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The assymmetry factor (See Figure 6) should be between 0.8 and 2.0. The assymmetry factor for any polar or reactive compounds should be determined using the process described above. If peaks are observed that exceed the peak width or assymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and is necessary. Some laboratories may chose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7). Such schemes cannot be conducted by placing the substances onto Tenax because many of the compounds (e.g. acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax.

14.4.3 The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.1 or 12.1.3.

S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required.

In general the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio, from the total ion current response, of approximately 5.

14.4.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.

14.4.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g. perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than $\pm$ 2 standard deviations from the mean (calculated

excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

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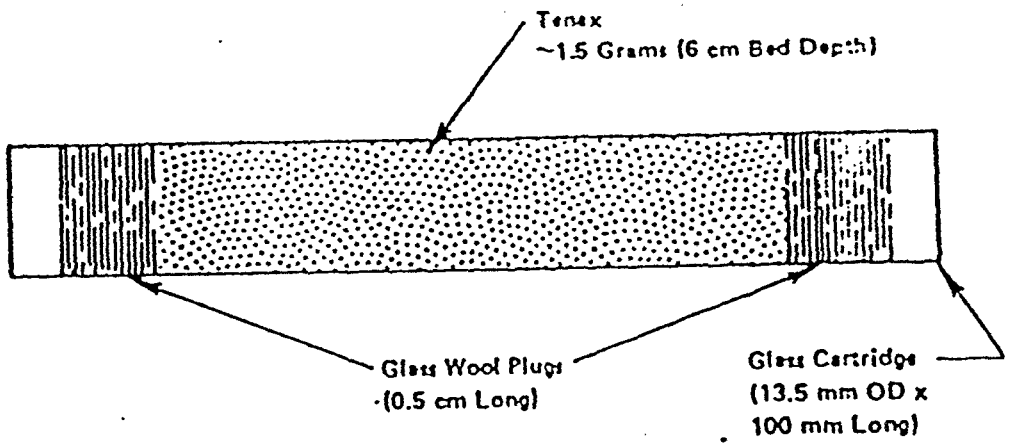
TABLE 1. RETENTION VOLUME ESTIMATES FOR COMPOUNDS ON TENAX

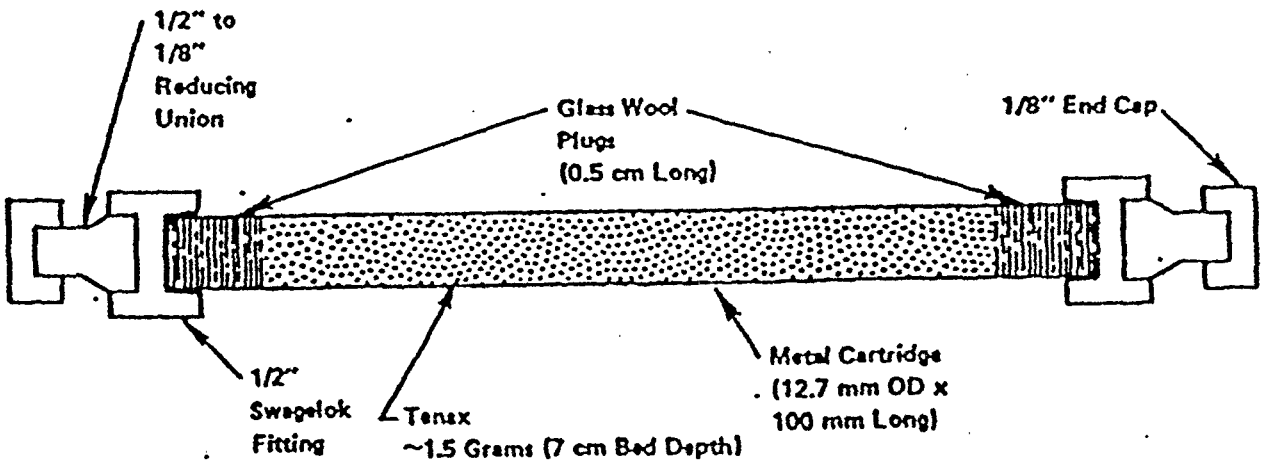
COMPOUND	ESTIMATED RETENTION VOLUME AT 100°F (38°C)-LITERS/GRAM
Benzene	19
Toluene	97
Ethyl Benzene	200
Xylene(s)	~ 200
Cumene	440
n-Heptane	20
1-Heptene	40
Chloroform	8
Carbon Tetrachloride	8
1,2-Dichloroethane	10
1,1,1-Trichloroethane	6
Tetrachloroethylene	80
Trichloroethylene	20
1,2-Dichloropropane	30
1,3-Dichloropropane	90
Chlorobenzene	150
Bromoform	100
Ethylene Dibromide	60
Bromobenzene	300

TABLE 2. SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION

M/E	% RELATIVE ABUNDANCE
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

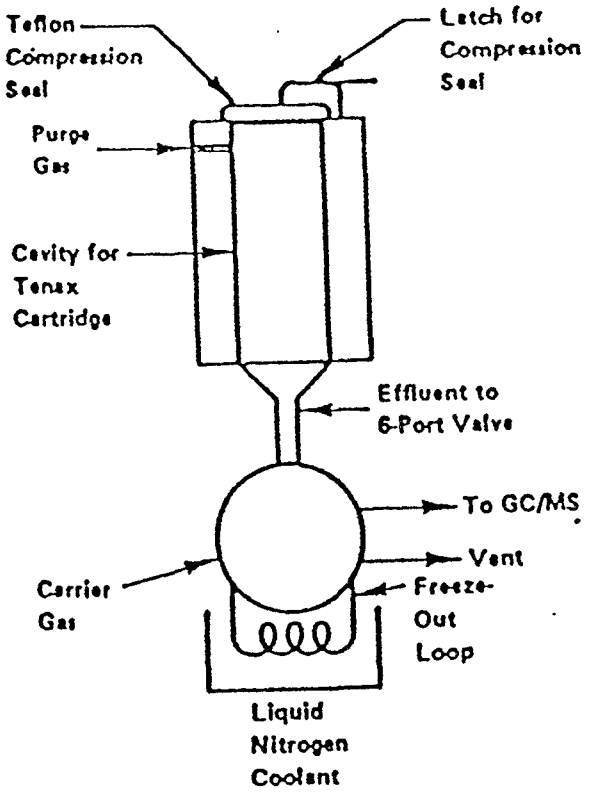


(a) Glass Cartridge

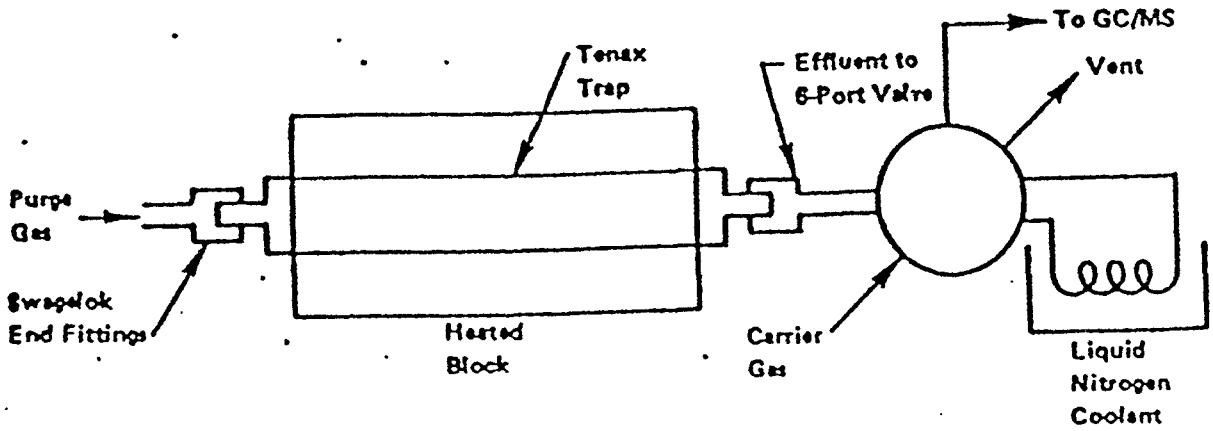


(b) Metal Cartridge

FIGURE 1. TENAX CARTRIDGE DESIGNS

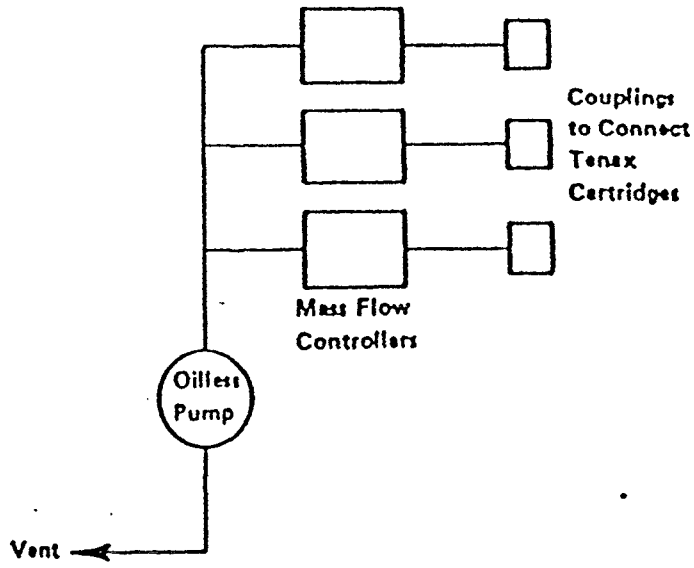


(a) Glass Cartridges (Compression Fit)

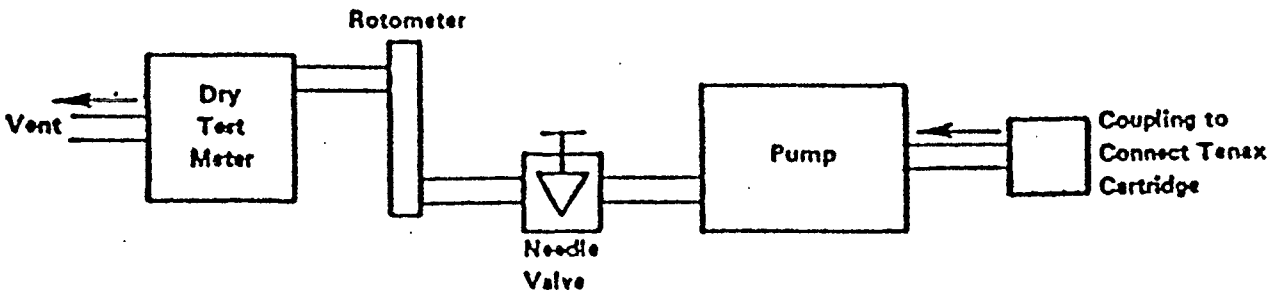


(b) Metal Cartridges (Swagelok Fittings)

FIGURE 2. TENAX CARTRIDGE DESORPTION MODULES



(a) Mass Flow Control



(b) Needle Valve Control

FIGURE 3. TYPICAL SAMPLING SYSTEM CONFIGURATIONS

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

PROJECT:_____ DATE(S) SAMPLED:_____

SITE:_____ TIME PERIOD SAMPLED:_____

LOCATION:_____ OPERATOR:_____

INSTRUMENT MODEL NO:_____ CALIBRATED BY:_____

PUMP SERIAL NO:_____

SAMPLING DATA

Sample Number:_____

Start Time: _____ Stop Time: _____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q ml/Min	Ambient Temperature °C	Barometric Pressure, mmHg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = _____ Liters

$$= \frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_ \text{ Liters}$$

* Flowrate from rotameter or soap bubble calibrator (specify which).
** Use data from dry gas meter if available.

FIGURE 4. EXAMPLE SAMPLING DATA SHEET

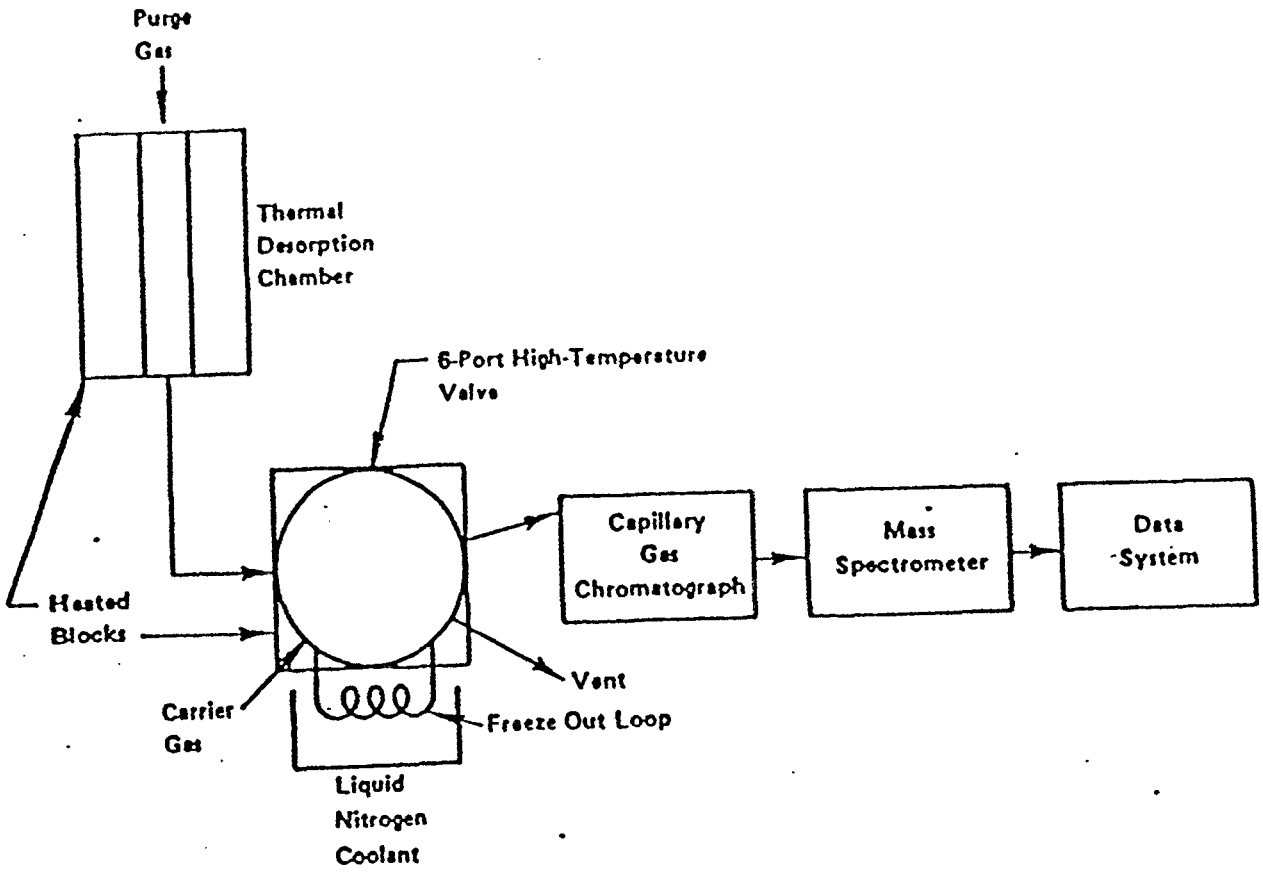
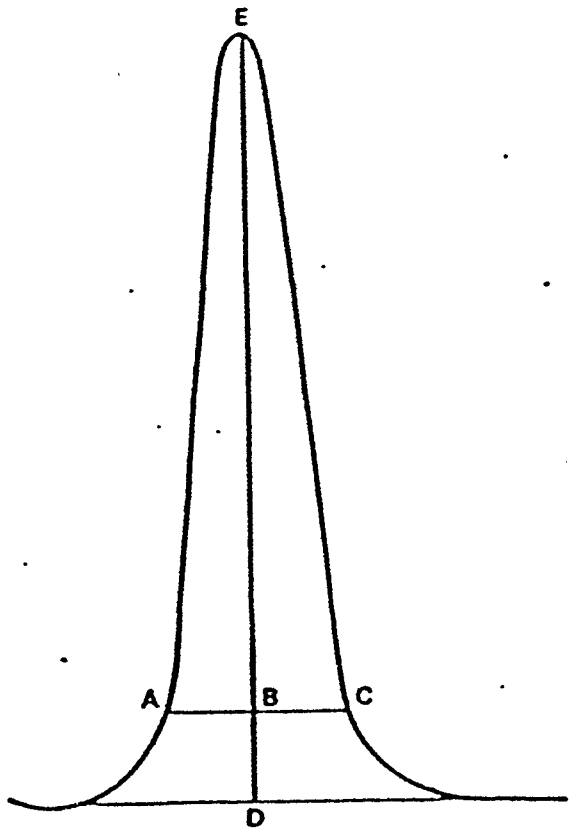


FIGURE 5. BLOCK DIAGRAM OF ANALYTICAL SYSTEM



$$\text{Asymmetry Factor} = \frac{BC}{AB}$$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Asymmetry Factor = $\frac{12}{11}$ = 1.1

FIGURE 6. PEAK ASYMMETRY CALCULATION

TABLE 2. LIST OF COMPOUNDS OF PRIMARY INTEREST

Compound	Applicable Method(s)	Comments
Acetaldehyde	TO-5	
Acrolein	TO-5	
Acrylonitrile	TO-2, TO-3	TO-3 yields better recovery data than TO-2.
Allyl Chloride	TO-2, TO-3	TO-3 yields better recovery data than TO-2.
Benzaldehyde	TO-5	
Benzene	TO-1, TO-2, TO-3	TO-3 yields best recovery data.
Benzyl Chloride	TO-1, TO-3	
Carbon Tetrachloride	(TO-1?) TO-2, TO-3	Breakthrough volume is very low using TO-1.
Chlorobenzene	TO-1, TO-3	
Chloroform	(TO-1?) TO-2, TO-3	Breakthrough volume is very low using TO-1.
Chloroprene (2-Chloro-1,3-butadiene)	TO-1, TO-3	The applicability of these methods for chloroprene has not been documented.
4,4'-DDE	TO-4	
4,4'-DDT	TO-4	
1,4-Dichlorobenzene	TO-1, TO-3	
Ethylene dichloride (1,2-Dichloroethane)	(TO-1?) TO-2, TO-3	Breakthrough volume very low using TO-1.
Formaldehyde	TO-5	
Methyl Chloroform (1,1,1-Trichloroethane)	(TO-1?) TO-2, TO-3	Breakthrough volume very low using TO-1.
Methylene chloride	TO-2, TO-3	
Nitrobenzene	TO-1, TO-3	
Perchloroethylene (Tetrachloroethylene)	TO-1, (TO-2?), TO-3	TO-2 performance has not been documented for this compound.
Polychlorinated biphenyls (PCBs)	TO-4	
Propanal	TO-5	
Toluene	TO-1, TO-2, TO-3	

TABLE 2. (Continued)

Compound	Applicable Method(s)	Comments
ichloroethylene	TO-1, TO-2, TO-3	
yl Chloride	TO-2, TO-3	
ylidine Chloride (1,1-dichloroethene)	TO-2, TO-3	
,p-Xylene	TO-1, TO-3	

APPENDIX B

EPA REFERENCE METHOD FOR THE DETERMINATION OF LEAD IN SUSPENDED PARTICULATE MATTER COLLECTED FROM AMBIENT AIR

The Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method)

1.0 *Applicability.*

1.1 This method provides a measurement of the mass concentration of total suspended particulate matter (TSP) in ambient air for determining compliance with the primary and secondary national ambient air quality standards for particulate matter as specified in § 50.6 and § 50.7 of this chapter. The measurement process is nondestructive, and the size of the sample collected is usually adequate for subsequent chemical analysis. Quality assurance procedures and guidance are provided in Part 58, Appendixes A and B, of this chapter and in References 1 and 2.

2.0 *Principle.*

2.1 An air sampler, properly located at the measurement site, draws a measured quantity of ambient air into a covered housing and through a filter during a 24-hr (nominal) sampling period. The sampler flow rate and the geometry of the shelter favor the collection of particles up to 25-50 μm (aerodynamic diameter), depending on wind speed and direction.(3) The filters used are specified to have a minimum collection efficiency of 99 percent for 0.3 μm (DOP) particles (see Section 7.1.4).

2.2 The filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain. The total volume of air sampled, corrected to EPA standard conditions (25° C, 760 mm Hg [101 kPa]), is determined from the measured flow rate and the sampling time. The concentration of total suspended particulate matter in the ambient air is computed as the mass of collected particles divided by the volume of air sampled, corrected to standard conditions, and is expressed in micrograms per standard cubic meter (μg/std m³). For samples collected at temperatures and pressures significantly different than standard conditions, these corrected concentrations may differ substantially from actual concentrations (micrograms per actual cubic meter), particularly at high elevations. The actual particulate matter concentration can be calculated from the corrected concentration using the actual temperature and pressure during the sampling period.

3.0 *Range.*

3.1 The approximate concentration range of the method is 2 to 750 μg/std m³. The upper limit is determined by the point at which the sampler can no longer maintain the specified flow rate due to the increased pressure drop of the loaded filter. This point is affected by particle size distribution, moisture content of the collected [illegible] from [illegible] to fil[illegible] among other things. The lower limit is determined by the sensitivity of the balance (see Section 7.10) and by inherent sources of error (see Section 6).

3.2 At wind speeds between 1.3 and 4.5 m/sec (3 and 10 mph), the high-volume air sampler has been found to collect particles up to 25 to 50 μm, depending on wind speed and direction.(3) For the filter specified in Section 7.1, there is effectively no lower limit on the particle size collected.

4.0 *Precision.*

4.1 Based upon collaborative testing, the relative standard deviation (coefficient of variation) for single analyst precision (repeatability) of the method is 3.0 percent. The corresponding value for interlaboratory precision (reproducibility) is 3.7 percent.(4)

5.0 *Accuracy.*

5.1 The absolute accuracy of the method is undefined because of the complex nature of atmospheric particulate matter and the difficulty in determining the "true" particulate matter concentration. This method provides a measure of particulate matter concentration suitable for the purpose specified under Section 1.0, Applicability.

6.0 *Inherent Sources of Error.*

6.1 *Airflow variation.* The weight of material collected on the filter represents the (integrated) sum of the product of the instantaneous flow rate times the instantaneous particle concentration. Therefore, dividing this weight by the average flow rate over the sampling period yields the true particulate matter concentration only when the flow rate is constant over the period. The error resulting from a nonconstant flow rate depends on the magnitude of the instantaneous changes in the flow rate and in the particulate matter concentration. Normally, such errors are not large, but they can be greatly reduced by equipping the sampler with an automatic flow controlling mechanism that maintains constant flow during the sampling period. Use of a constant flow controller is recommended.*

6.2 *Air volume measurement.* If the flow rate changes substantially or nonuniformly during the sampling period, appreciable error in the estimated air volume may result from using the average of the presampling and postsampling flow rates. Greater air volume measurement accuracy may be achieved by (1) equipping the sampler with a flow controlling mechanism that maintains constant air flow during the sampling period,* (2) using a calibrated, continuous flow rate recording device to record the

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*At elevated altitudes, the effectiveness of automatic flow controllers may be reduced because of a reduction in the maximum sampler flow.

t pr[illegible]. Two [illegible] devices are shown in gures 2a and 2b. Figure 2a shows multiple ed resistance plates, which necessitate assembly of the unit each time the flow istance is changed. A preferable design, istrated in Figure 2b, has a variable flow triction that can be adjusted externally thout disassembly of the unit. Use of a nventional, orifice-type transfer standard assumed in the calibration procedure ection 9). However, the use of other types transfer standards meeting the above ecifications, such as the one shown in gure 2c, may be approved; see the note llowing Section 9.1.

.9 *Filter conditioning environment*

.9.1 *Controlled temperature:* between 15° d 30° C with less than ±3° C variation ring equilibration period.

.9.2 *Controlled humidity:* Less than 50 rcent relative humidity, constant within percent.

.10 *Analytical balance.*

.10.1 *Sensitivity:* 0.1 mg.

.10.2 Weighing chamber designed to ept an unfolded 20.3 x 25.4 cm (8 x 10 in) er.

.11 *Area light source,* similar to X-ray n viewer, to backlight filters for visual in- ction.

.12 *Numbering device,* capable of print- identification numbers on the filters fore they are placed in the filter condi- ning environment, if not numbered by supplier.

.0 *Procedure.*

(See References 1 and 2 for quality assurce information.)

.1 Number each filter, if not already mbered, near its edge with a unique iden- ication number.

.2 Backlight each filter and inspect for holes, particles, and other imperfections; ers with visible imperfections must not used.

.3 Equilibrate each filter in the condi- ning environment for at least 24-hr.

.4 Following equilibration, weigh each er to the nearest milligram and record s tare weight (W_i) with the filter identifi- ion number.

.5 Do not bend or fold the filter before lection of the sample.

.6 Open the shelter and install a num- ed, preweighed filter in the sampler, fol- ving the sampler manufacturer's instruc- ns. During inclement weather, precau- ns must be taken while changing filters prevent damage to the clean filter and s of sample from or damage to the ex- sed filter. Filter cassettes that can be ded and unloaded in the laboratory may used to minimize this problem (See Sec- n 6.6).

[redacted] for at least 5 min to establish run-temperature conditions.

8.8 Record the flow indicator reading and, if needed, the barometric pressure (P_a) and the ambient temperature (T_a) see NOTE following step 8.12). Stop the sampler. Determine the sampler flow rate (see Section 10.1); if it is outside the acceptable range (1.1 to 1.7 m³/min [39–60 ft³/min]), use a different filter, or adjust the sampler flow rate. Warning: Substantial flow adjustments may affect the calibration of the orifice-type flow indicators and may necessitate recalibration.

8.9 Record the sampler identification information (filter number, site location or identification number, sample date, and starting time).

8.10 Set the timer to start and stop the sampler such that the sampler runs 24-hrs, from midnight to midnight (local time).

8.11 As soon as practical following the sampling period, run the sampler for at least 5 min to again establish run-temperature conditions.

8.12 Record the flow indicator reading and, if needed, the barometric pressure (P_a) and the ambient temperature (T_a).

NOTE: No onsite pressure or temperature measurements are necessary if the sampler flow indicator does not require pressure or temperature corrections (e.g., a mass flowmeter) or if average barometric pressure and seasonal average temperature for the site are incorporated into the sampler calibration (see step 9.3.9). For individual pressure and temperature corrections, the ambient pressure and temperature can be obtained by onsite measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampler site and the airport. For samplers having flow recorders but not constant flow controllers, the average temperature and pressure at the site *during the sampling period* should be estimated from weather bureau or other available data.

8.13 Stop the sampler and carefully remove the filter, following the sampler manufacturer's instructions. Touch only the outer edges of the filter. See the precautions in step 8.6.

8.14 Fold the filter in half lengthwise so that only surfaces with collected particulate matter are in contact and place it in the filter holder (glassine envelope or manila folder).

8.15 Record the ending time or elapsed time on the filter information record, either from the stop set-point time, from an elapsed time indicator, or from a continuous

[redacted] 1,440 ± 60 min. for a valid sample.

8.16 Record on the filter information record any other factors, such as meteorological conditions, construction activity, fires or dust storms, etc., that might be pertinent to the measurement. If the sample is known to be defective, void it at this time.

8.17 Equilibrate the exposed filter in the conditioning environment for at least 24-hrs.

8.18 Immediately after equilibration, reweigh the filter to the nearest milligram and record the gross weight with the filter identification number. See Section 10 for TSP concentration calculations.

9.0 *Calibration.*

9.1 Calibration of the high volume sampler's flow indicating or control device is necessary to establish traceability of the field measurement to a primary standard via a flow rate transfer standard. Figure 3a illustrates the certification of the flow rate transfer standard and Figure 3b illustrates its use in calibrating a sampler flow indicator. Determination of the corrected flow rate from the sampler flow indicator, illustrated in Figure 3c, is addressed in Section 10.1

NOTE: The following calibration procedure applies to a conventional orifice-type flow transfer standard and an orifice-type flow indicator in the sampler (the most common types). For samplers using a pressure recorder having a square-root scale, 3 other acceptable calibration procedures are provided in Reference 12. Other types of transfer standards may be used if the manufacturer or user provides an appropriately modified calibration procedure that has been approved by EPA under Section 2.8 of Appendix C to Part 58 of this chapter.

9.2 *Certification of the flow rate transfer standard.*

9.2.1 *Equipment required:* Positive displacement standard volume meter traceable to the National Bureau of Standards (such as a Roots meter or equivalent), stop-watch, manometer, thermometer, and barometer.

9.2.2 Connect the flow rate transfer standard to the inlet of the standard volume meter. Connect the manometer to measure the pressure at the inlet of the standard volume meter. Connect the orifice manometer to the pressure tap on the transfer standard. Connect a high-volume air pump (such as a high-volume sampler blower) to the outlet side of the standard volume meter. See Figure 3a.

9.2.3 Check for leaks by temporarily clamping both manometer lines (to avoid fluid loss) and blocking the orifice with a large-diameter rubber stopper, wide cellophane tape, or other suitable means. Start the high-volume air pump and note any change in the standard volume meter read- [redacted] the reading changes, locate any leaks by listening for a whistling sound and/or retightening all connections, making sure that all gaskets are properly installed.

9.2.4 After satisfactorily completing the leak check as described above, unclamp both manometer lines and zero both manometers.

9.2.5 Achieve the appropriate flow rate through the system, either by means of the variable flow resistance in the transfer standard or by varying the voltage to the air pump. (Use of resistance plates as shown in Figure 1a is discouraged because the above leak check must be repeated each time a new resistance plate is installed.) At least five different but constant flow rates, evenly distributed, with at least three in the specified flow rate interval (1.1 to 1.7 m³/min [39–60 ft³/min]), are required.

9.2.6 Measure and record the certification data on a form similar to the one illustrated in Figure 4 according to the following steps.

9.2.7 Observe the barometric pressure and record as P_i (item 8 in Figure 4).

9.2.8 Read the ambient temperature in the vicinity of the standard volume meter and record it as T_i (item 9 in Figure 4).

9.2.9 Start the blower motor, adjust the flow, and allow the system to run for at least 1 min for a constant motor speed to be attained.

9.2.10 Observe the standard volume meter reading and simultaneously start a stopwatch. Record the initial meter reading (V_i) in column 1 of Figure 4.

9.2.11 Maintain this constant flow rate until at least 3 m³ of air have passed through the standard volume meter. Record the standard volume meter inlet pressure manometer reading as ΔP (column 5 in Figure 4), and the orifice manometer reading as ΔH (column 7 in Figure 4). Be sure to indicate the correct units of measurement.

9.2.12 After at least 3 m³ of air have passed through the system, observe the standard volume meter reading while simultaneously stopping the stopwatch. Record the final meter reading (V_f) in column 2 and the elapsed time (t) in column 3 of Figure 4.

9.2.13 Calculate the volume measured by the standard volume meter at meter conditions of temperature and pressures as $V_m = V_f - V_i$. Record in column 4 of Figure 4.

9.2.14 Correct this volume to standard volume (std m³) as follows:

$$V_{std} = V_m \frac{P_i - \Delta P}{P_{std}} \frac{T_{std}}{T_i}$$

where:

V_{std} = standard volume, std m³;

ard [redacted] he m[redacted]

= barometric pressure during calibration, mm Hg or kPa;

= differential pre[redacted] inlet to volume meter, mm Hg or kPa;

= 760 mm Hg or 101 kPa;

= 298 K;

= ambient temperature during calibration, K.

culate the standard flow rate (std m³/min) as follows:

$$Q_{std} = \frac{V_{std}}{t}$$

re:

= standard volumetric flow rate, std m³/min

lapsed time, minutes.

ecord Q_{std} to the nearest 0.01 std m³/min olumn 6 of Figure 4.

2.15 Repeat steps 9.2.9 through 9.2.14 at least four additional constant flow s, evenly spaced over the approximate ge of 1.0 to 1.8 std m³/min (35–64 ft³/).

2.16 For each flow, compute

$\Delta H (P_1/P_{std})(298/T_1)$

umn 7a of Figure 4) and plot these value inst Q_{std} as shown in Figure 3a. Be sure se consistent units (mm Hg or kPa) for metric pressure. Draw the orifice trans- standard certification curve or calculate linear least squares slope (m) and inter- (b) of the certification curve:

$\Delta H (P_1/P_{std})(298/T_1)$

$Q_{std}+b$. See Figures 3 and 4. A certifica- graph should be readable to 0.02 std min.

2.17 Recalibrate the transfer standard ually or as required by applicable qual- control procedures. (See Reference 2.)

3 *Calibration of sampler flow indica-*

OTE: For samplers equipped with a flow rolling device, the flow controller must isabled to allow flow changes during ration of the sampler's flow indicator. he alternate calibration of the flow con- er given in 9.4 may be used. For sam- s using an orifice-type flow indicator nstream of the motor, do not vary the rate by adjusting the voltage or power lied to the sampler.

1 A form similar to the one illustrated igure 5 should be used to record the ration data.

2 Connect the transfer standard to inlet of the sampler. Connect the orifice ometer to the orifice pressure tap, as il- rated in Figure 3b. Make sure there are [redacted] the sampler.

9.3.3 Operate the sampler for at least 5 minutes to establish thermal equilibrium prior to the calibration.

9.3.4 Measure and record the ambient temperature, T_a, and the barometric pressure, P_a, during calibration.

9.3.5 Adjust the variable resistance or, if applicable, insert the appropriate resistance plate (or no plate) to achieve the desired flow rate.

9.3.6 Let the sampler run for at least 2 min to re-establish the run-temperature conditions. Read and record the pressure drop across the orifice (ΔH) and the sampler flow rate indication (I) in the appropriate columns of Figure 5.

9.3.7 Calculate $\sqrt{\Delta H(P_a/P_{std})(298/T_a)}$ and determine the flow rate at standard conditions (Q_{std}) either graphically from the certification curve or by calculating Q_{std} from the least square slope and intercept of the transfer standard's transposed certification curve: $Q_{std} = 1/m \sqrt{\Delta H(P_a/P_{std})(298/T_a)} - b$. Record the value of Q_{std} on Figure 5.

9.3.8 Repeat steps 9.3.5, 9.3.6, and 9.3.7 for several additional flow rates distributed over a range that includes 1.1 to 1.7 std m³/min.

9.3.9 Determine the calibration curve by plotting values of the appropriate expression involving I, selected from Table 1, against Q_{std}. The choice of expression from Table 1 depends on the flow rate measurement device used (see Section 7.4.1) and also on whether the calibration curve is to incorporate geographic average barometric pressure (P_a) and seasonal average temperature (T_a) for the site to approximate actual pressure and temperature. Where P_a and T_a can be determined for a site for a seasonal period such that the actual barometric pressure and temperature at the site do not vary by more than ±60 mm Hg (8 kPa) from P_a or ±15° C from T_a, respectively, then using P_a and T_a avoids the need for subsequent pressure and temperature calculation when the sampler is used. The geographic average barometric pressure (P_a) may be estimated from an altitude-pressure table or by making an (approximate) elevation correction of −26 mm Hg (−3.46 kPa) for each 305 m (1,000 ft) above sea level (760 mm Hg or 101 kPa). The seasonal average temperature (T_a) may be estimated from weather station or other records. Be sure to use consistent units (mm Hg or kPa) for barometric pressure.

9.3.10 Draw the sampler calibration curve or calculate the linear least squares slope (m), intercept (b), and correlation coefficient of the calibration curve: [Expression from Table 1] = $mQ_{std}+b$. See Figures 3 and 5. Calibration curves should be readable to 0.02 std m³/min.

[redacted] flow controller, the flow controlling mechanism should be re-enabled and set to a flow near the lower flow limit to allow maximum control range. The sample flow rate should be verified at this time with a clean filter installed. Then add two or more filters to the sampler to see if the flow controller maintains a constant flow; this is particularly important at high altitudes where the range of the flow controller may be reduced.

9.4 Alternate calibration of flow-controlled samplers. A flow-controlled sampler may be calibrated solely at its controlled flow rate, provided that previous operating history of the sampler demonstrates that the flow rate is stable and reliable. In this case, the flow indicator may remain uncali- [redacted] relative change between initial and final flows, and the sampler should be recalibrated more often to minimize potential loss of samples because of controller malfunction.

9.4.1 Set the flow controller for a flow near the lower limit of the flow range to allow maximum control range.

9.4.2 Install a clean filter in the sampler and carry out steps 9.3.2, 9.3.3, 9.3.4, 9.3.6, and 9.3.7.

9.4.3 Following calibration, add one or two additional clean filters to the sampler, reconnect the transfer standard, and operate the sampler to verify that the controller maintains the same calibrated flow rate; this is particularly important at high altitudes where the flow control range may be reduced.

TABLE 1. EXPRESSIONS FOR PLOTTING SAMPLER CALIBRATION CURVES

Type of sampler flow rate measuring device	Expression: For actual pressure and temperature corrections	Expression: For incorporation of geographic average pressure and seasonal average temperature
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
Rotameter, or orifice and pressure recorder having square root scale*	$I\sqrt{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$I\sqrt{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.

DURING SAMPLER OPERATION

Type of sampler flow rate measuring device	Expression: For actual pressure and temperature corrections	Expression: For use when geographic average pressure and seasonal average temperature have been incorporated into the sampler calibration
...lass flowmeter	I	I
...rifice and pressure indicator	$\sqrt{I\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	$\sqrt{I}$
...otameter, or orifice and pressure recorder having square root scale*	$I\sqrt{\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	I

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.

10.0 *Calculations of TSP Concentration.*

10.1 Determine the average sampler flow ...te during the sampling period according ...either 10.1.1 or 10.1.2 below.

10.1.1 For a sampler without a continu...s flow recorder, determine the appropri...e expression to be used from Table 2 cor...sponding to the one from Table 1 used in ...ep 9.3.9. Using this appropriate expres...on, determine Q_{std} for the initial flow rate ...om the sampler calibration curve, either ...aphically or from the transposed regres...n equation:

$$I =$$

...m ([Appropriate expression from Table ...-b)

...nilarly, determine Q_{std} from the final flow ...ading, and calculate the average flow Q_{std} ...one-half the sum of the initial and final ...w rates.

...0.1.2 For a sampler with a continuous ...w recorder, determine the average flow ...e device reading, I, for the period. Deter...ne the appropriate expression from Table ...corresponding to the one from Table 1 ...ed in step 9.3.9. Then using this expres...n and the average ... ...ate reading, de...mine Q_{std} from ... ...pler calibration ...ve, either graphically or from the trans...ed regression equation:

$$I =$$

...n ([Appropriate expression from Table ...-b)

If the trace shows substantial flow change during the sampling period, greater accuracy may be achieved by dividing the sampling period into intervals and calculating an average reading before determining Q_{std}.

10.2 Calculate the total air volume sampled as:

$$V = Q_{std} \times t$$

where:

V = total air volume sampled, in standard volume units, std m^3;

Q_{std} = average standard flow rate, std m^3/min;

t = sampling time, min.

10.3 Calculate and report the particulate matter concentration as:

$$TSP = \frac{(W_f - W_i) \times 10^6}{V}$$

where:

TSP = mass concentration of total suspended particulate matter, $\mu g/std\ m^3$;

W_i = initial weight of clean filter, g;

W_f = final weight of exposed filter, g;

V = air volume sampled, converted to standard conditions, std m^3,

10^6 = conversion of g to μg.

10.4 If desired, the actual particulate matter concentration (see Section 2.2) can be calculated as follows:

$(TSP)_a = TSP\ (P_3/P_{std})(298/T_3)$

...hen...

$(TSP)_a$ = actual concentration at field conditions, $\mu g/m^3$;

TSP = concentration at standard conditions, $\mu g/std\ m^3$;

P_3 = average barometric pressure during sampling period, mm Hg;

P_{std} = 760 mn Hg (or 101 kPa);

T_3 = average ambient temperature during sampling period, K.

11.0 *References.*

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2. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Specific Methods. EPA-600/4-77-027a, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1977.

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...PA T... roced... or D... ning pH and Integrity of High-Volume Air Filters. QAD/M-80.01. Available from the Methods Standardization Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory (MD-77), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1980.

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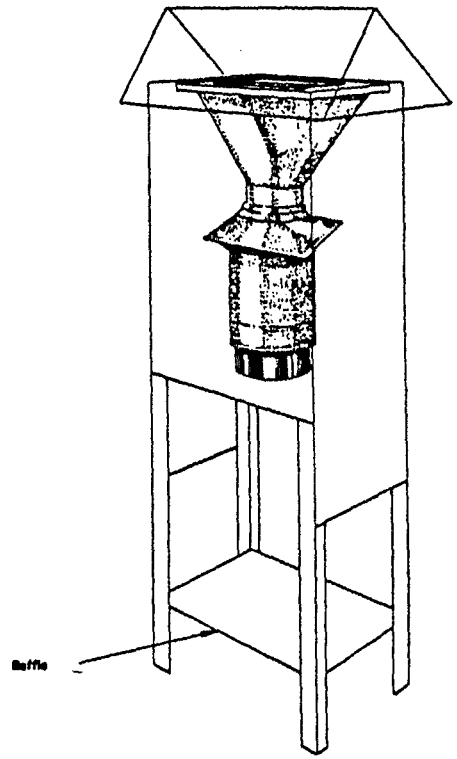
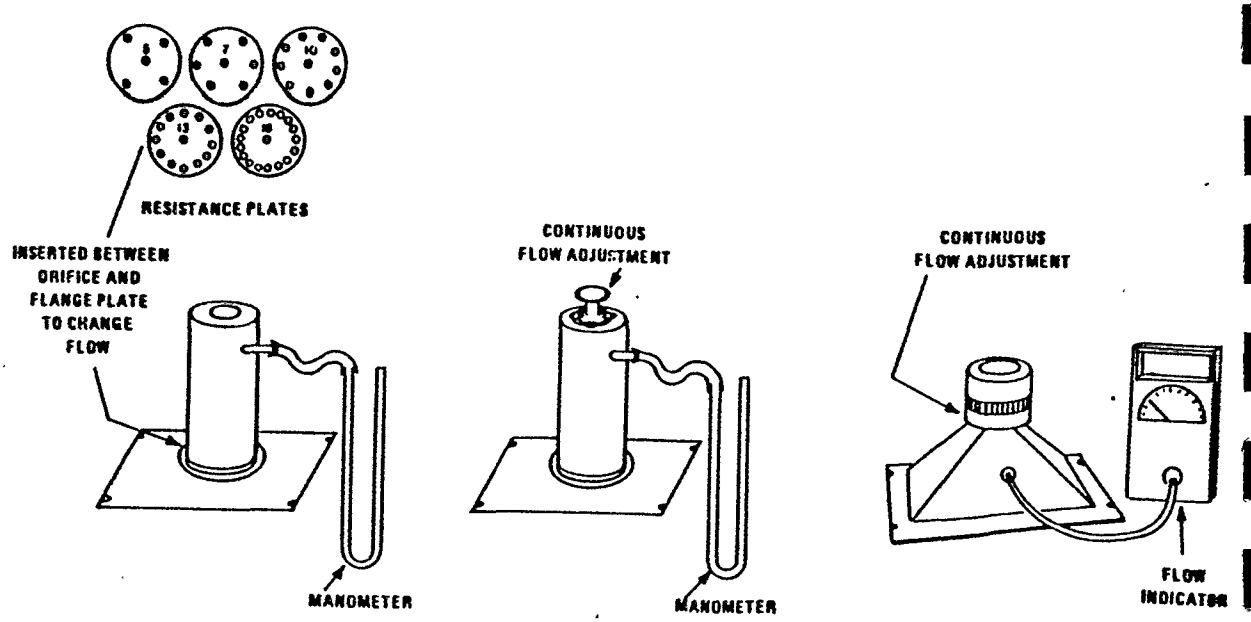


Figure 1. High-volume sampler in shelter.



2a. ORIFICE UNIT USING FIXED RESISTANCE PLATES.

2b. PREFERABLE ORIFICE UNIT WITH EXTERNALLY ADJUSTABLE RESISTANCE.

2c. ELECTRONIC FLOWMETER WITH EXTERNAL ADJUSTABLE RESISTANCE.

Figure 2. Various types of flow transfer standards. Note that all devices are designed to mount to the filter inlet area of the sampler.

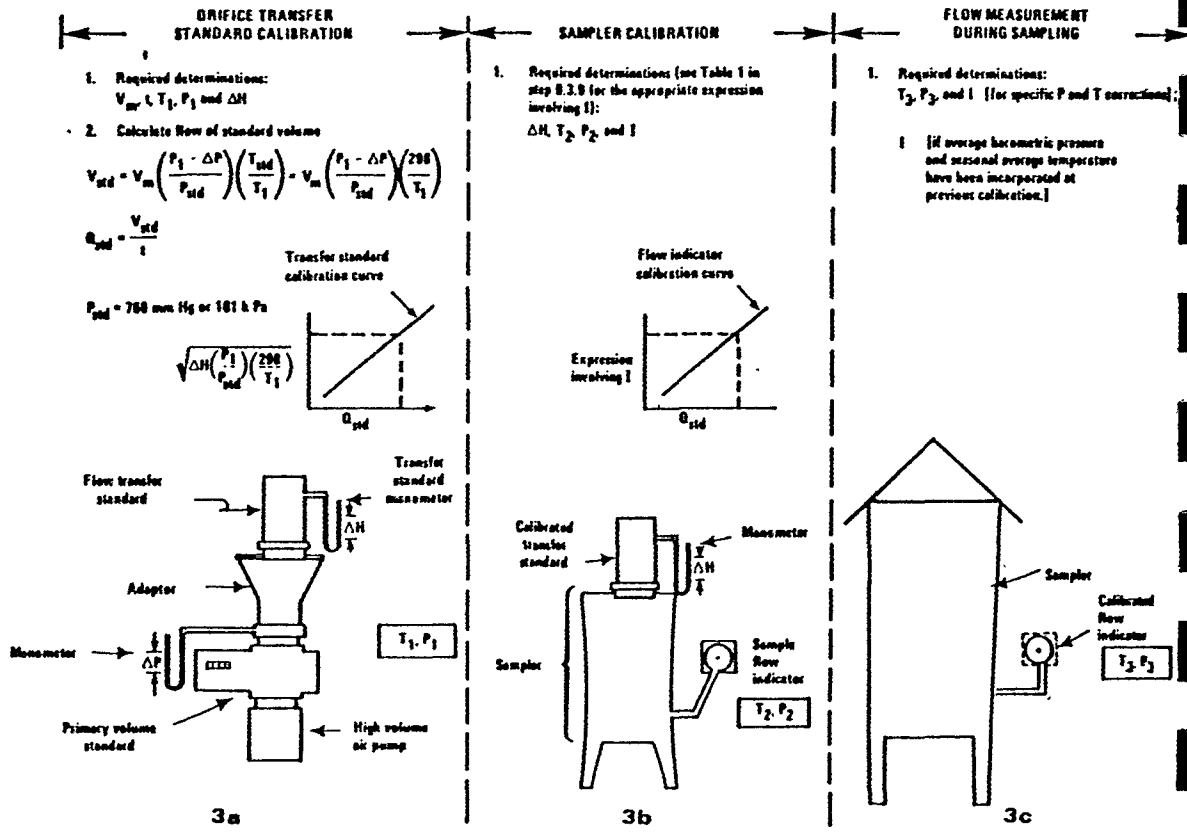


Figure 3. Illustration of the 3 steps in the flow measurement process.

ORIFICE TRANSFER STANDARD CERTIFICATION WORKSHEET

Run No.	(1) Meter reading start V_i (m^3)	(2) Meter reading stop V_f (m^3)	(3) Sampling time t (min)	(4) Volume measured V_m (m^3)	(5) Differential pressure (at inlet to volume meter) ΔP (mm Hg or kPa)	(6) (X) Flow rate Q_{std} (std m^3/min)	(7) Pressure drop across orifice ΔH ☐(in) or ☐(cm) of water	(7a) (Y) $\sqrt{\Delta H\left(\frac{P_1}{P_{std}}\right)\left(\frac{298}{T_1}\right)}$
1								
2								
3								
4								
5								
6								

RECORDED CALIBRATION DATA

Standard volume meter no. _____

Transfer standard type: ☐ orifice ☐ other

Model No. _____ Serial No. _____

(8) P_1: _____ mm Hg (or kPa) (10) P_{std}: 760 mm Hg (or 101 kPa)

(9) T_1: _____ K (11) T_{std}: 298 K

Calibration performed by: _____

Date: _____

CALCULATION EQUATIONS

(1) $V_m = V_f - V_i$

(2) $V_{std} = V_m\left(\frac{P_1 - \Delta P}{P_{std}}\right)\left(\frac{T_{std}}{T_1}\right)$

(3) $Q_{std} = \frac{V_{std}}{t}$

LEAST SQUARES CALCULATIONS

Linear ($Y = mX + b$) regression equation of $Y = \sqrt{\Delta H(P_1/P_{std})(298/T_1)}$ on $X = Q_{std}$ for Orifice Calibration Unit (i.e., $\sqrt{\Delta H(P_1/P_{std})(298/T_1)} = mQ_{std} + b$)

Slope (m) = _____ Intercept (b) = _____ Correlation coefficient (r) = _____

To use for subsequent calibration: $X = \frac{1}{m}(Y-b)$; $\boxed{Q_{std} = \frac{1}{m}\left(\sqrt{\Delta H\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)} - b\right)}$

Figure 4. Example of orifice transfer standard certification worksheet.

HIGH-VOLUME AIR SAMPLER CALIBRATION WORKSHEET

Site Location: _____

Date: _____ Barometric Pressure, P_2 mm Hg (or kPa) _____

Calibrated By: _____ Temperature, T_2 (K) _____

Sampler No. _____ Serial No. _____

Transfer std. type: _____ Serial No. _____

P_{std} = 760 mm Hg (or 101 kPa)

Optional:

Average barometric pressure: P_a = _____

Seasonal average temperature: T_a = _____

No.	ΔH Pressure drop across orifice ☐(in) or ☐(cm) of water	$\sqrt{\Delta H\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	(X) Q_{std} (from orifice certification) std m^3/min	I Sampler flow rate indication (arbitrary)	(Y) For specific pressure and temperature corrections (see Table 1) ☐ I or ☐ $I\sqrt{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$ or ☐ $I\sqrt{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	(Y) For incorporation of average pressure and seasonal average temperature (see Table 1) ☐ I or ☐ $I\sqrt{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$ or ☐ $I\sqrt{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
1						
2						
3						
4						
5						
6						

LEAST SQUARES CALCULATIONS

Linear regression of Y on X: $Y = mX + b$; Y = appropriate expression from Table 1; $X = Q_{std}$

Slope (m) = ____ Intercept (b) = ____ Correlation Coeff. (r) = _____

To determine subsequent flow rate during use: $X = \frac{1}{m}(Y-b)$; $\boxed{Q_{std} = \frac{1}{m}(\text{[Appropriate expression from Table 2]} - b)}$

Figure 5. Example of high-volume air sampler calibration worksheet.

[47 FR 54912, Dec. 6, 1982; 48 FR 17355, Apr. 22, 1983]

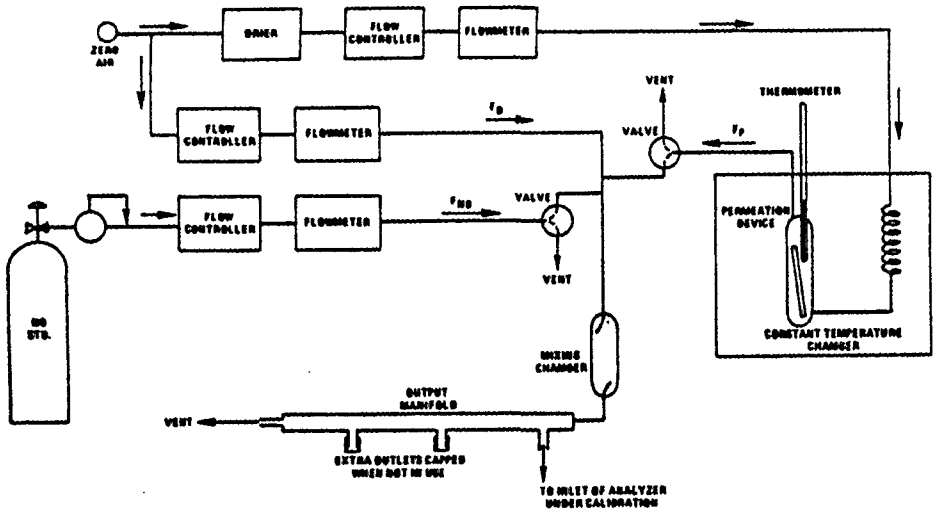


Figure 2. Schematic diagram of a typical calibration apparatus using an NO_2 permeation device.

[41 FR 52688, Dec. 1, 1976, as amended at 48 FR 2529, Jan 20, 1983]

Appendix G to Part 50—Reference Method for the Determination of Lead in Suspended Particulate Matter Collected From Ambient Air

1. *Principle and applicability.*

1.1 Ambient air suspended particulate matter is collected on a glass-fiber filter for 24 hours using a high volume air sampler. The analysis of the 24-hour samples may be performed for either individual samples or composites of the samples collected over a calendar month or quarter, provided that the compositing procedure has been approved in accordance with section 2.8 of Appendix C to Part 58 of this chapter—*Modifications of methods by users.* (Guidance or assistance in requesting approval under Section 2.8 can be obtained from the address given in section 2.7 of Appendix C to Part 58 of this chapter.)

1.2 Lead in the particulate matter is solubilized by extraction with nitric acid (HNO_3), facilitated by heat or by a mixture of HNO_3 and hydrochloric acid (HCl) facilitated by ultrasonication.

1.3 The lead content of the sample is analyzed by atomic absorption spectrometry using an air-acetylene flame, the 283.3 or 217.0 nm lead absorption line, and the optimum instrumental conditions recommended by the manufacturer.

1.4 The ultrasonication extraction with HNO_3/HCl will extract metals other than lead from ambient particulate matter.

2. *Range, sensitivity, and lower detectable limit.* The values given below are typical of the methods capabilities. Absolute values will vary for individual situations depending on the type of instrument used, the lead line, and operating conditions.

2.1 *Range.* The typical range of the method is 0.07 to 7.5 μg Pb/m³ assuming an upper linear range of analysis of 15 μg/ml and an air volume of 2,400 m³.

2.2 *Sensitivity.* Typical sensitivities for a 1 percent change in absorption (0.0044 absorbance units) are 0.2 and 0.5 μg Pb/ml for the 217.0 and 283.3 nm lines, respectively.

2.3 *Lower detectable limit (LDL).* A typical LDL is 0.07 μg Pb/m³. The above value was calculated by doubling the between-laboratory standard deviation obtained for the lowest measurable lead concentration in a collaborative test of the method.(*15*) An air volume of 2,400 m³ was assumed.

3. *Interferences.* Two types of interferences are possible: chemical and light scattering.

3.1 *Chemical.* Reports on the absence (*1, 2, 3, 4, 5*) of chemical interferences far outweigh those reporting their presence, (*6*) therefore, no correction for chemical interferences is given here. If the analyst suspects that the sample matrix is causing a chemical interference, the interference can be verified and corrected for by carrying out the analysis with and without the method of standard additions.(*7*)

3.2 *Light scattering.* Nonatomic absorption or light scattering, produced by high concentrations of dissolved solids in the sample, can produce a significant interference, especially at low lead concentrations. (*2*) The interference is greater at the 217.0 nm line than at the 283.3 nm line. No interference was observed using the 283.3 nm line with a similar method.(*1*)

Light scattering interferences can, however, be corrected for instrumentally. Since the dissolved solids can vary depending on the origin of the sample, the correction may be necessary, especially when using the 217.0 nm line. Dual beam instruments with a continuum source give the most accurate correction. A less accurate correction can be obtained by using a nonabsorbing lead line that is near the lead analytical line. Information on use of these correction techniques can be obtained from instrument manufacturers' manuals.

If instrumental correction is not feasible, the interference can be eliminated by use of the ammonium pyrrolidinecarbodithioate-methylisobutyl ketone, chelation-solvent extraction technique of sample preparation.(*8*)

4. *Precision and bias.*

4.1 The high-volume sampling procedure used to collect ambient air particulate matter has a between-laboratory relative standard deviation of 3.7 percent over the range 80 to 125 μg/m³.(*9*) The combined extraction-analysis procedure has an average within-laboratory relative standard deviation of 5 to 6 percent over the range 1.5 to 15 μg Pb/ml, and an average between laboratory relative standard deviation of 7 to 9 percent over the same range. These values include use of either extraction procedure.

4.2 Single laboratory experiments and collaborative testing indicate that there is no significant difference in lead recovery between the hot and ultrasonic extraction procedures.(*15*)

5. *Apparatus.*

5.1 *Sampling.*

5.1.1 *High-Volume Sampler.* Use and calibrate the sampler as described in Appendix B to this part.

5.2 *Analysis.*

5.2.1 *Atomic absorption spectrophotometer.* Equipped with lead hollow cathode or electrodeless discharge lamp.

5.2.1.1 *Acetylene.* The grade recommended by the instrument manufacturer should be used. Change cylinder when pressure drops below 50-100 psig.

5.2.1.2 *Air.* Filtered to remove particulate, oil, and water.

5.2.2 *Glassware.* Class A borosilicate glassware should be used throughout the analysis.

5.2.2.1 *Beakers.* 30 and 150 ml. graduated, Pyrex.

5.2.2.2 *Volumetric flasks.* 100-ml.

5.2.2.3 *Pipettes.* To deliver 50, 30, 15, 8, 4, 2, 1 ml.

5.2.2.4 *Cleaning.* All glassware should be scrupulously cleaned. The following procedure is suggested. Wash with laboratory detergent, rinse, soak for 4 hours in 20 percent (w/w) HNO_3, rinse 3 times with distilled-deionized water, and dry in a dust free manner.

5.2.3 *Hot plate.*

5.2.4. *Ultrasonication water bath, unheated.* Commercially available laboratory ultrasonic cleaning baths of 450 watts or higher "cleaning power," i.e., actual ultrasonic power output to the bath have been found satisfactory.

5.2.5 *Template.* To aid in sectioning the glass-fiber filter. See figure 1 for dimensions.

5.2.6 *Pizza cutter.* Thin wheel. Thickness 1mm.

5.2.7 *Watch glass.*

5.2.8 *Polyethylene bottles.* For storage of samples. Linear polyethylene gives better storage stability than other polyethylenes and is preferred.

5.2.9 Parafilm "M" [1] American Can Co., Marathon Produ[illegible]ch, Wis., or equivalent.

6. *Reagents.*

6.1 *Sampling.*

6.1.1 *Glass fiber filters.* The specifications given below are intended to aid the user in obtaining high quality filters with reproducible properties. These specifications have been met by EPA contractors.

6.1.1.1 *Lead content.* The absolute lead content of filters is not critical, but low values are, of course, desirable. EPA typically obtains filters with a lead content of 75 μg/filter.

It is important that the variation in lead content from filter to filter, within a given batch, be small.

6.1.1.2 *Testing.*

6.1.1.2.1 For large batches of filters (>500 filters) select at random 20 to 30 filters from a given batch. For small batches (>500 filters) a lesser number of filters may be taken. Cut one ¾"x8" strip from each filter anywhere in the filter. Analyze all strips, separately, according to the directions in sections 7 and 8.

6.1.1.2.2 Calculate the total lead in each filter as

[1] Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

$$F_b = \mu g\ Pb/ml \times \frac{100\ ml}{strip} \times \frac{12\ strips}{filter}$$

where:

F_b = Amount of lead per 72 square inches of filter, μg.

6.1.1.2.3 Calculate the mean, F_b, of the values and the relative standard deviation (standard deviation/mean × 100). If the relative standard deviation is high enough so that, in the analysts opinion, subtraction of F_b, (section 10.3) may result in a significant error in the μg Pb/m² the batch should be rejected.

6.1.1.2.4 For acceptable batches, use the value of F_b to correct all lead analyses (section 10.3) of particulate matter collected using that batch of filters. If the analyses are below the LDL (section 2.3) no correction is necessary.

6.2 *Analysis.*

6.2.1 Concentrated (15.6 *M*) HNO_3. ACS reagent grade HNO_3 and commercially available redistilled HNO_3 has found to have sufficiently low lead concentrations.

6.2.2 Concentrated (11.7 *M*) HCl. ACS reagent grade.

6.2.3 *Distilled-deionized water.* (D.I. water).

6.2.4 3 *M* HNO_3. This solution is used in the hot extraction procedure. To prepare, add 192 ml of concentrated HNO_3 to D.I. water in a 1 *l* volumetric flask. Shake well, cool, and dilute to volume with D.I. water. *Caution:* Nitric acid fumes are toxic. Prepare in a well ventilated fume hood.

6.2.5 0.45 *M* HNO_3. This solution is used as the matrix for calibration standards when using the hot extraction procedure. To prepare, add 29 ml of concentrated HNO_3 to D.I. water in a 1 *l* volumetric flask. Shake well, cool, and dilute to volume with D.I. water.

6.2.6 2.6 *M* HNO_3+0 to 0.9 *M* HCl. This solution is used in the ultrasonic extraction procedure. The concentration of HCl can be varied from 0 to 0.9 *M*. Directions are given for preparation of a 2.6 *M* HNO_3+0.9 *M* HCl solution. Place 167 ml of concentrated HNO_3 into a 1 *l* volumetric flask and add 77 ml of concentrated HCl. Stir 4 to 6 hours, dilute to nearly 1 *l* with D.I. water, cool to room temperature, and dilute to 1 *l*.

6.2.7 0.40 *M* HNO_3 + X *M* HCl. This solution is used as the matrix for calibration standards when using the ultrasonic extraction procedure. To prepare, add 26 ml of concentrated HNO_3, plus the ml of HCl required, to a 1 *l* volumetric flask. Dilute to nearly 1 *l* with D.I. water, cool to room temperature, and dilute to 1 *l*. The amount of HCl required can be determined from the following equation:

$$y = \frac{77\ ml \times 0.15 \times x}{0.9M}$$

where:

y = ml of concentrated HCl required.
x = molarity of HCl in 6.2.6.
0.15 = dilution factor in 7.2.2.

6.2.8 Lead nitrate, $Pb(NO_3)_2$. ACS reagent grade, purity 99.0 percent. Heat for 4 hours at 120° C and cool in a desiccator.

6.3 *Calibration standards.*

6.3.1 Master standard, 1000 μg Pb/ml in HNO_3. Dissolve 1.598 g of $Pb(NO_3)_2$ in 0.45 *M* HNO_3 contained in a 1 *l* volumetric flask and dilute to volume with 0.45 *M* HNO_3.

6.3.2 Master standard, 1000 μg Pb/ml in HNO_3/HCl. Prepare as in section 6.3.1 except use the HNO_3/HCl solution in section 6.2.7.

Store standards in a polyethylene bottle. Commercially available certified lead standard solutions may also be used.

7. *Procedure.*

7.1 *Sampling.* Collect samples for 24 hours using the procedure described in reference *10* with glass-fiber filters meeting the specifications in section 6.1.1. Transport collected samples to the laboratory taking care to minimize contamination and loss of sample. (*16*).

7.2 *Sample preparation.*

7.2.1 *Hot extraction procedure.*

7.2.1.1 Cut a ¾" x 8" strip from the exposed filter using a template and a pizza cutter as described in Figures 1 and 2. Other cutting procedures may be used.

Lead in ambient particulate matter collected on glass fiber filters has been shown to be uniformly distributed across the filter.[1, 3, 11] Another study [12] has shown that when sampling near a roadway, strip position contributes significantly to the overall variability associated with lead analyses. Therefore, when sampling near a roadway, additional strips should be analyzed to minimize this variability.

7.2.1.2 Fold the strip in half twice and place in a 150-ml beaker. Add 15 ml of 3 *M* HNO_3 to cover the sample. The acid should completely cover the sample. Cover the beaker with a watch glass.

7.2.1.3 Place beaker on the hot-plate, contained in a fume hood, and boil gently for 30 min. Do not let the sample evaporate to dryness. *Caution:* Nitric acid fumes are toxic.

7.2.1.4 Remove beaker from hot plate and cool to near room temperature.

7.2.1.5 Quantitatively transfer the sample as follows:

7.2.1.5.1 Rinse watch glass and sides of beaker with D.I. water.

7.2.1.5.2 Decant extract and rinsings into a 100-ml volumetric flask.

7.2.1.5.3 Add D.I. water to 40 ml mark on beaker, cover with watch glass, and set aside for a minimum of 30 minutes. This is a critical step and cannot be omitted since it allows the HNO_3 trapped in the filter to diffuse into the rinse water.

7.2.1.5.4 Decant the water from the filter into the volumetric flask.

7.2.1.5.5 Rinse filter and beaker twice with D.I. water and add rinsings to volumetric flask until total volume is 80 to 85 ml.

7.2.1.5.6 Stopper flask and shake vigorously. Set aside for approximately 5 minutes or until foam has dissipated.

7.2.1.5.7 Bring solution to volume with D.I. water. Mix thoroughly.

7.2.1.5.8 Allow solution to settle for one hour before proceeding with analysis.

7.2.1.5.9 If sample is to be stored for subsequent analysis, transfer to a linear polyethylene bottle.

7.2.2 *Ultrasonic extraction procedure.*

7.2.2.1 Cut a ¾" x 8" strip from the exposed filter as described in section 7.2.1.1.

7.2.2.2 Fold the strip in half twice and place in a 30 ml beaker. Add 15 ml of the HNO_3/HCl solution in section 6.2.6. The acid should completely cover the sample. Cover the beaker with parafilm.

The parafilm should be placed over the beaker such that none of the parafilm is in contact with water in the ultrasonic bath. Otherwise, rinsing of the parafilm (section 7.2.2.4.1) may contaminate the sample.

7.2.2.3 Place the beaker in the ultrasonication bath and operate for 30 minutes.

7.2.2.4 Quantitatively transfer the sample as follows:

7.2.2.4.1 Rinse parafilm and sides of beaker with D.I. water.

7.2.2.4.2 Decant extract and rinsings into a 100 ml volumetric flask.

7.2.2.4.3 Add 20 ml D.I. water to cover the filter strip, cover with parafilm, and set aside for a minimum of 30 minutes. This is a critical step and cannot be omitted. The sample is then processed as in sections 7.2.1.5.4 through 7.2.1.5.9.

NOTE: Samples prepared by the hot extraction procedure are now in 0.45 *M* HNO_3. Samples prepared by the ultrasonication procedure are in 0.40 *M* HNO_3 + X *M* HCl.

8. *Analysis.*

8.1 Set the wavelength of the monochromator at 283.3 or 217.0 nm. Set or align other instrumental operating conditions as recommended by the manufacturer.

8.2 The sample can be analyzed direct from the volumetric flask, or an appropria amount of sample decanted into a samp analysis tube. In either case, care should taken not to disturb the settled solids.

8.3 Aspirate samples, calibration stan ards and blanks (section 9.2) into the flar and record the equilibrium absorbance.

8.4 Determine the lead concentration μg Pb/ml, from the calibration curve, se tion 9.3.

8.5 Samples that exceed the linear ca bration range should be diluted with acid the same concentration as the calibrati standards and reanalyzed.

9. *Calibration.*

9.1 Working standard, 20 μg Pb/ml. Pr pared by diluting 2.0 ml of the mast standard (section 6.3.1 if the hot acid e traction was used or section 6.3.2 if the t trasonic extraction procedure was used) 100 ml with acid of the same concentrati as used in preparing the master standard.

9.2 *Calibration standards.* Prepare dai by diluting the working standard, with t same acid matrix, as indicated below. Oth lead concentrations may be used.

Volume of 20 μg/ml working standard, ml	Final volume, ml	Concentration μg Pb/ml
0	100	
1.0	200	
2.0	200	
2.0	100	
4.0	100	
6.0	100	
15.0	100	
30.0	100	
50.0	100	
100.0	100	

9.3 *Preparation of calibration curv* Since the working range of analysis wi vary depending on which lead line is use and the type of instrument, no one set of i structions for preparation of a calibratio curve can be given. Select standards (plu the reagent blank), in the same acid concer tration as the samples, to cover the linea absorption range indicated by the instru ment manufacturer. Measure the abso bance of the blank and standards as in se tion 8.0. Repeat until good agreement is ob tained between replicates. Plot absorbanc (y-axis) versus concentration in μg Pb/m (x-axis). Draw (or compute) a straight lin through the linear portion of the curve. D not force the calibration curve throug zero. Other calibration procedures may b used.

To determine stability of the calibratio curve, remeasure—alternately—one of th following calibration standards for ever 10th sample analyzed: Concentration ≅ 1μ

Pb/ml; concentration ≦ 10 μg Pb/ml. If either standard deviates by more than 5 percent from the value predicted by the calibration curve, recalibrate and repeat the previous 10 analyses.

10. *Calculation.*

10.1 *Measured air volume.* Calculate the measured air volume at Standard Temperature and Pressure as described in Reference 10.

10.2 *Lead concentration.* Calculate lead concentration in the air sample.

$$C = \frac{(\mu g\ Pb/ml \times 100\ ml/strip \times 12\ strips/filter) - F_b}{V_{STP}}$$

where:

C=Concentration, μg Pb/sm³.
μg Pb/ml=Lead concentration determined from section 8.
100 ml/strip=Total sample volume.
12 strips=Total useable filter area, 8" × 9". Exposed area of one strip, ¾" × 7".
Filter=Total area of one strip, ¾" × 8".
F_b=Lead concentration of blank filter, μg, from section 6.1.1.2.3.
V_{STP}=Air volume from section 10.2.

11. *Quality control.*

¾" × 8" glass fiber filter strips containing 80 to 2000 μg Pb/strip (as lead salts) and blank strips with zero Pb content should be used to determine if the method—as being used—has any bias. Quality control charts should be established to monitor differences between measured and true values. The frequency of such checks will depend on the local quality control program.

To minimize the possibility of generating unreliable data, the user should follow practices established for assuring the quality of air pollution data, (*13*) and take part in EPA's semiannual audit program for lead analyses.

12. *Trouble shooting.*

1. During extraction of lead by the hot extraction procedure, it is important to keep the sample covered so that corrosion products—formed on fume hood surfaces which may contain lead—are not deposited in the extract.

2. The sample acid concentration should minimize corrosion of the nebulizer. However, different nebulizers may require lower acid concentrations. Lower concentrations can be used provided samples and standards have the same acid concentration.

3. Ashing of particulate samples has been found, by EPA and contractor laboratories, to be unnecessary in lead analyses by atomic absorption. Therefore, this step was omitted from the method.

4. Filtration of extracted samples, to remove particulate matter, was specifically excluded from sample preparation, because some analysts have observed losses of lead due to filtration.

5. If suspended solids should clog the nebulizer during analysis of samples, centrifuge the sample to remove the solids.

13. *Authority.*

(Secs. 109 and 301(a), Clean Air Act, as amended (42 U.S.C. 7409, 7601(a)))

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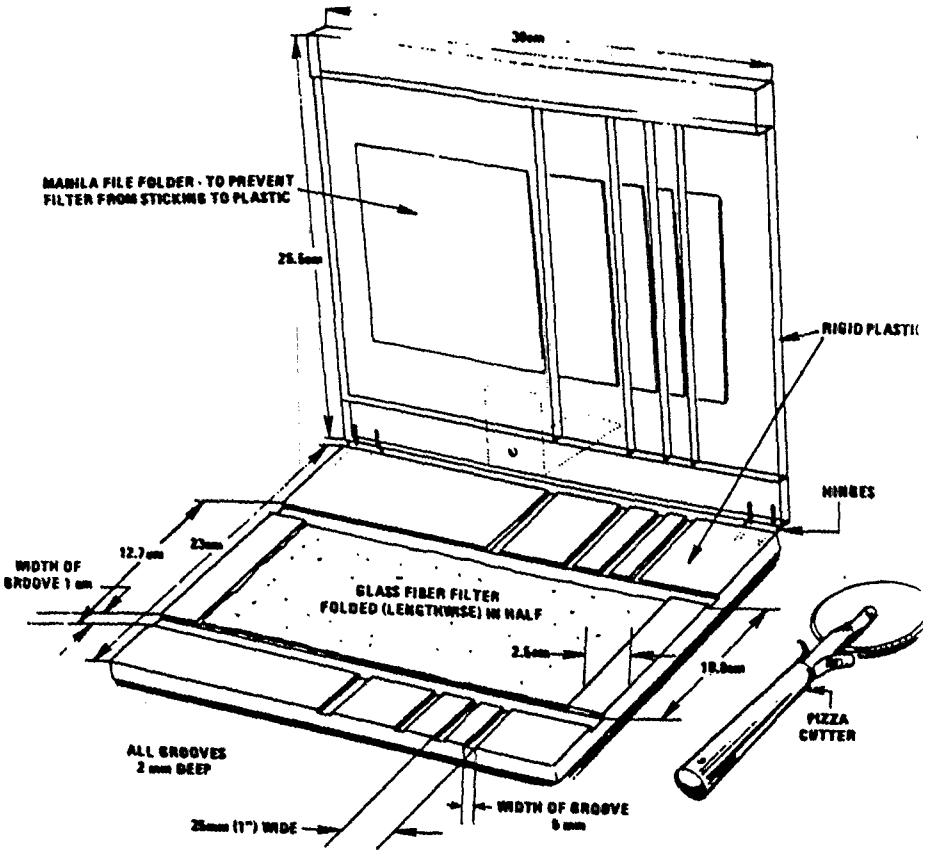

Figure 1

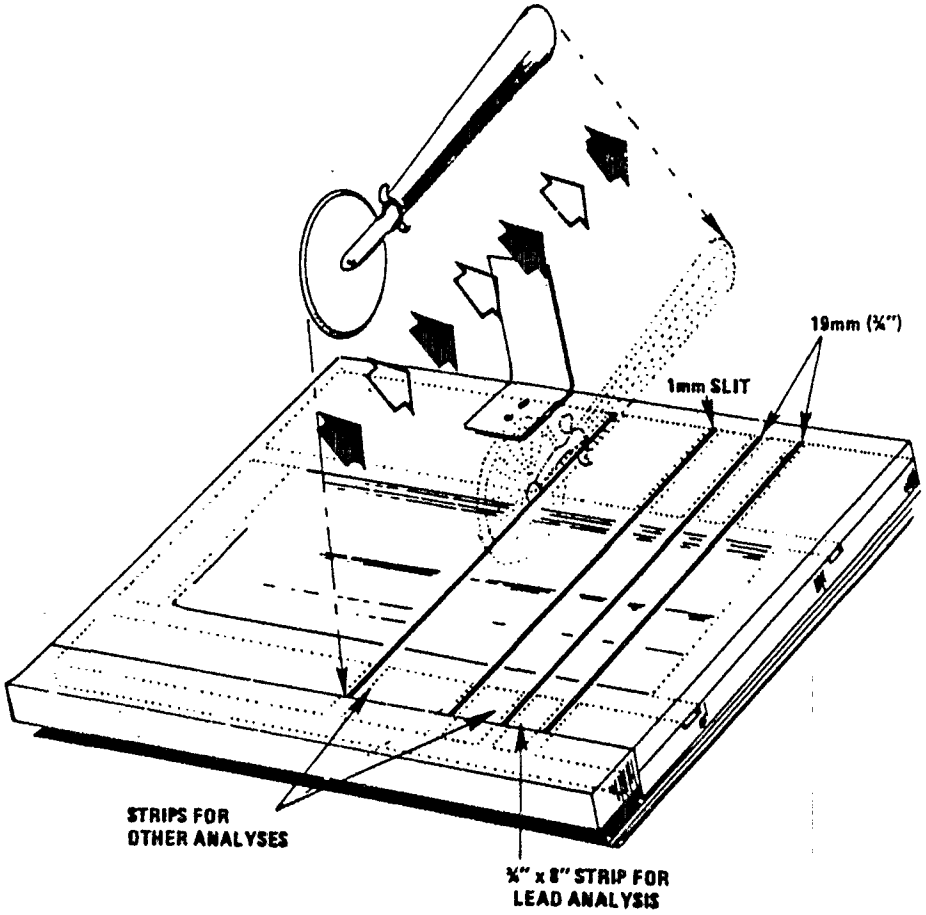

Figure 2

(Secs. 109, 301(a) of the Clean Air Act, as amended (42 U.S.C. 7409, 7601(a)); secs. 110, 301(a) and 319 of the Clean Air Act (42 U.S.C. 7410, 7601(a), 7619))

[43 FR 46258, Oct. 5, 1978; 44 FR 37915, June 29, 1979, as amended at 46 FR 44163, Sept. 3, 1981; 52 FR 24664, July 1, 1987]

Appendix H to Part 50—Interpretation of the National Ambient Air Quality Standards for Ozone

1. *General*

This appendix explains how to determine when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm (235 $\mu g/m^3$) is equal to or less than 1. An expanded discussion of these procedures and associated examples are contained in the "Guideline for Interpretation of Ozone Air Quality Standards." For purposes of clarity in the following discussion, it is convenient to use the term "exceedance" to describe a daily maximum hourly average ozone measurement that is greater than the level of the standard. Therefore, the phrase "expected number of days with maximum hourly average ozone concentrations above the level of the standard" may be simply stated as the "expected number of exceedances."

The basic principle in making this determination is relatively straightforward. Most of the complications that arise in determining the expected number of annual exceedances relate to accounting for incomplete sampling. In general, the average number of exceedances per calendar year must be less than or equal to 1. In its simplest form, the number of exceedances at a monitoring site would be recorded for each calendar year and then averaged over the past 3 calendar years to determine if this average is less than or equal to 1.

2. *Interpretation of Expected Exceedances*

The ozone standard states that the expected number of exceedances per year must be less than or equal to 1. The statistical term "expected number" is basically an arithmetic average. The following example explains what it would mean for an area to be in compliance with this type of standard. Suppose a monitoring station records a valid daily maximum hourly average ozone value for every day of the year during the past 3 years. At the end of each year, the number of days with maximum hourly concentrations above 0.12 ppm is determined and this number is averaged with the results of previous years. As long as this average remains "less than or equal to 1," the area is in compliance.

3. *Estimating the Number of Exceedances for a Year*

In general, a valid daily maximum hourly average value may not be available for each day of the year, and it will be necessary to account for these missing values when estimating the number of exceedances for a particular calendar year. The purpose of these computations is to determine if the expected number of exceedances per year is less than or equal to 1. Thus, if a site has two or more observed exceedances each year, the standard is not met and it is not necessary to use the procedures of this section to account for incomplete sampling.

The term "missing value" is used here in the general sense to describe all days that do not have an associated ozone measurement. In some cases, a measurement might actually have been missed but in other cases no measurement may have been scheduled for that day. A daily maximum ozone value is defined to be the highest hourly ozone value recorded for the day. This daily maximum value is considered to be valid if 75 percent of the hours from 9:01 a.m. to 9:00 p.m. (LST) were measured or if the highest hour is greater than the level of the standard.

In some areas, the seasonal pattern of ozone is so pronounced that entire months need not be sampled because it is extre unlikely that the standard would be ex ed. Any such waiver of the ozone mor ing requirement would be handled u provisions of 40 CFR, Part 58. Some a ance should also be made for days for w valid daily maximum hourly values wer obtained but which would quite likely been below the standard. Such an allow introduces a complication in that it bec necessary to define under what conditi missing value may be assumed to have less than the level of the standard. Th lowing criterion may be used for ozone:

A missing daily maximum ozone v may be assumed to be less than the lev the standard if the valid daily maxim both the preceding day and the follo day do not exceed 75 percent of the lev the standard.

Let z denote the number of missing maximum values that may be assumed less than the standard. Then the follo formula shall be used to estimate th pected number of exceedances for the

$$e = v + [(v/n)8(N-n-z)] \quad (1$$

(*Indicates multiplication.)

where:

e=the estimated number of exceeda for the year,
N=the number of required monitc days in the year,
n=the number of valid daily maxima,
v=the number of daily values above level of the standard, and
z=the number of days assumed to be than the standard level.

This estimated number of exceeda shall be rounded to one decimal place (tional parts equal to 0.05 round up).

It should be noted that N will be the number of days in the year unless the propriate Regional Administrator has gr ed a waiver under the provisions of 40 Part 58.

The above equation may be interprete tuitively in the following manner. The mated number of exceedances is equa the observed number of exceedances plus an increment that accounts for inc plete sampling. There were (N-n) mis values for the a certain numb these, namely z, were assumed to be than the standard. Therefore, (N-n-z) r ing values are considered to include pos exceedances. The fraction of meas values that are above the level of the st ard is v/n. It is assumed that this same tion applies to the (N-n-z) missing va and that (v/n)*(N-n-z) of these values w also have exceeded the level of the st ard.

APPENDIX C

EPA METHOD TO13

METHOD T013

DETERMINATION OF BENZO(a)PYRENE [B(a)P] AND OTHER POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN AMBIENT AIR USING GAS CHROMATOGRAPHIC (GC) AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC (HPLC) ANALYSIS

Revision 1.0
June, 1988

1. Scope

1.1 Polynuclear aromatic hydrocarbons (PAHs) have received increased attention in recent years in air pollution studies because some of these compounds are highly carcinogenic or mutagenic. In particular, benzo[a]pyrene (B[a]P) has been identified as being highly carcinogenic. To understand the extent of human exposure to B[a]P, and other PAHs, a reliable sampling and analytical method has been established. This document describes a sampling and analysis procedure for B[a]P and other PAHs involving a combination quartz filter/adsorbent cartridge with subsequent analysis by gas chromatography (GC) with flame ionization (FI) and mass spectrometry (MS) detection (GC/FI and GC/MS) or high resolution liquid chromatography (HPLC). The analytical methods are a modification of EPA Test Method 610 and 625, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, and Methods 8000, 8270, and 8310, Test Methods for Evaluation of Solid Waste.

1.2 Fluorescence methods were among the very first methods used for detection of B[a]P and other PAHs as a carcinogenic constituent of coal tar (1-7). Fluorescent methods are capable of measuring subnanogram quantities of PAHs, but tend to be fairly non-selective. The normal spectra obtained tended to be intense and lacked resolution. Efforts to overcome this difficulty led to the use of ultraviolet (UV) absorption spectroscopy as the detection method coupled with pre-speciated techniques involving liquid chromatography (LC) and thin layer chromatography (TLC) to isolate specific PAHs, particularly B[a]P (8). As with fluorescence spectroscopy, the individual spectra for various PAHs are unique, although portions of spectra for different compounds may be the same. As with fluoresence techniques, the possibility of spectra overlap required complete separation of sample components to insure accurate measurement of component levels. Hence, the use of UV absorption coupled

with pre-speciation involving LC and TLC and fluorescence spectroscopy has declined and is now being replaced with the more sensitive high performance liquid chromatography (9) with UV/fluorescence detection and highly sensitive and specific gas chromatograph with either flame ionization detector or coupled with mass spectroscopy (10-11).

1.3 The choice of GC and HPLC as the recommended procedures for analysis of B[a]P and other PAHs are influenced by their sensitivity and selectivity, along with their ability to analyze complex samples. This method provides for both GC and HPLC approaches to the determination of B[a]P and other PAHs in the extracted sample.

1.4 The analytical methodology is well defined, but the sampling procedures can reduce the validity of the analytical results. Recent studies (12-15) have indicated that non-volatile PAHs (vapor pressure $<10^{-8}$ mm Hg) may be trapped on the filter, but post-collection volatilization problems may distribute the PAHs down stream of the the filter to the back-up adsorbent. A wide variety of adsorbents such as Tenax GC, XAD-2 resin and polyurethane foam (PUF) have been used to sample B[a]P and other PAH vapors. All adsorbents have demonstrated high collection efficiency for B[a]P in particular. In general, XAD-2 resin has a higher collection efficiency (16-17) for volatile PAHs than PUF, as well as a higher retention efficiency. However, PUF cartridges are easier to handle in the field and maintain better flow characteristics during sampling. Likewise, PUF has demonstrated its capability in sampling organochlorine pesticides and polychlorinated biphenyls (Compendium Methods T04 and T010 respectively), and polychlorinated dibenzo-p-dioxins (Compendium Method T09). However, PUF has demonstrated a lower recovery efficiency and storage capability for naphthalene and B[a]P, respectively, than XAD-2. There have been no significant losses of PAHs, up to 30 days of storage at 0°C, using XAD-2. It also appears that XAD-2 resin has a higher collection efficiency for volatile PAHs than PUF, as well as a higher retention efficiency for both volatile and reactive PAHs. Consequently, while the literature cites weaknesses and strengths of using either XAD-2 or PUF, this method covers both the utilization of XAD-2 and PUF as the adsorbent to address post-collection volatilization problems associated with B[a]P and other reactive PAHs.

1.5 This method covers the determination of B[a]P specificially by both GC and HPLC and enables the qualitative and quantitative analysis of the other PAHs. They are:

Acenaphthene	Benzo(k)fluoranthene
Acenaphthylene	Chrysene
Anthracene	Dibenzo(a,h)anthracene
Benzo(a)anthracene	Fluoranthene
Benzo(a)pyrene	Fluorene
Benzo(b)fluoranthene	Indeno(1,2,3-cd)pyrene
Benzo(e)pyrene	Naphthalene
Benzo(g,h,i)perylene	Phenanthrene
	Pyrene

The GC and HPLC methods are applicable to the determination of PAHs compounds involving two-member rings or higher. Nitro-PAHs have not been fully evaluated using this procedure; therefore, they are not included in this method. When either of the methods are used to analyze unfamiliar samples for any or all of the compounds listed above, compound identification should be supported by both techniques.

1.6 With careful attention to reagent purity and optimized analytical conditions, the detection limits for GC and HPLC methods range from 1 ng to 10 pg which represents detection of B[a]P and other PAHs in filtered air at levels below 100 pg/m^3. To obtain this detection limit, at least 100 m^3 of air must be sampled.

2. Applicable Documents

2.1 ASTM Standards

2.1.1 Method D1356 - Definitions of Terms Relating to Atmospheric Sampling and Analysis.

2.1.2 Method E260 - Recommended Practice for General Gas Chromatography Procedures.

2.1.3 Method E355 - Practice for Gas Chromatography Terms and Relationships.

2.1.4 Method E682 - Practice for Liquid Chromatography Terms and Relationships.

2.1.5 Method D-1605-60 - Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors.

2.2 Other Documents

2.2.1 Existing Procedures (18-25)

2.2.2 Ambient Air Studies (26-28)

2.2.3 U.S. EPA Technical Assistance Document (29-32)

2.2.4 General Metal Works Operating Procedures for Model PS-1 Sampler, General Metal Works, Inc., Village of Cleves, Ohio.

3. Summary of Method

3.1 Filters and adsorbent cartridges (containing XAD-2 or PUF) are cleaned in solvents and vacuum-dried. The filters and adsorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on a modified high volume sampler.

3.2 Approximately 325 m^3 of ambient air is drawn through the filter and adsorbent cartridge using a calibrated General Metal Works Model PS-1 Sampler, or equivalent (breakthrough has not shown to be a problem with sampling volumes of 325 m^3).

3.3 The amount of air sampled through the filter and adsorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and adsorbent cartridges to the analytical laboratory for analysis.

3.4 The filters and adsorbent cartridge are extracted by Soxhlet extraction with appropriate solvent. The extract is concentrated by Kuderna-Danish (K-D) evaporator, followed by silica gel clean-up using column chromatography to remove potential interferences prior to analysis.

3.5 The eluate is further concentrated by K-D evaporator, then analyzed by either gas chromatograhy equipped with FI or MS detection or high performance liquid chromatography (HPLC). The analytical system is verified to be operating properly and calibrated with five concentration calibration solutions, each analyzed in triplicate.

3.6 A preliminary analysis of the sample extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If necessary, recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, etc.

3.7 The samples and the blanks are analyzed and used (along with the amount of air sampled) to calculated the concentratuon of B[a]P in ambient air.

3.8 Other PAHs can be determined both qualitatively and quantitatively through optimization of the GC or HPLC procedures.

4. Significance

4.1 Several documents have been published which describe sampling and analytical approaches for benzo[a]pyrene and other PAHs, as outlined in Section 2.2. The attractive features of these methods have been combined in this procedure. This method has been validated in the laboratory; however, one must use caution when employing it for specific applications.

4.2 The relatively low level of B[a]P and other PAHs in the environment requires use of high volume (~6.7 cfm) sampling techniques to acquire sufficient sample for analysis. However, the volatility of certain PAHs prevents efficient collection on filter media alone. Consequently, this method utilizes both a filter and a backup adsorbent cartridge which provide for efficient collection of most PAHs.

5. Definitions

Definitions used in this document and in any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, D1605-60, E260, and E255. All abbreviations and symbols are defined within this document at point of use.

5.1 Sampling efficiency (SE) - ability of the sampling medium to trap vapors of interest. %SE is the percentage of the analyte of interest colleted and retained by the sampling medium when it is introduced as a vapor in air or nitrogen into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use.

5.2 Retention time (RT) - time to elute a specific chemical from a chromatographic column. For a specific carrier gas flow rate, RT is measured from the time the chemical is injected into the gas stream until it appears at the detector.

5.3 High Performance Liquid Chromatography - an analytical method based on separation of compounds of a liquid mixture through a liquid chromatographic column and measuring the separated components with a suitable detector.

5.4 Gradient elution - defined as increasing the strength of the mobile phase during a chromatographic analysis. The net effect of gradient elution is to shorten the retention time of compounds strongly retained on the analytical column. Gradient elution may be stepwise on continuous.

5.5 Method detection limit (MDL) - the minimum concentration of a substance that can be measured and reported with confidence and that the value is above zero.

5.6 Kuderna-Danish apparatus - the Kuderna-Danish (KD) appartus is a system for concentrating materials dissolved in volatile solvents.

5.7 Reverse phase liquid chromatography - reverse phase liquid chromatography involves a non-polar absorbent (C-18,ODS) coupled with a polar solvent to separate non-polar compounds.

5.8 Guard column - guard columns in HPLC are usually short (5cm) columns attached after the injection port and before the analytial column to prevent particles and strongly retained compounds from accumulating on the analytical column. The guard column should always be the same stationary phase as the analytical column and is used to extend the life of the analytical column.

5.9 MS-SIM - the GC is coupled to a select ion mode (SIM) detector where the instrument is programmed to acquire data for only the target compounds and to disregard all others. This is performed using SIM coupled to retention time discriminators. The SIM analysis procedure provides quantitative results.

5.10 Sublimation - Sublimation is the direct passage of a substance from the solid state to the gaseous state and back into the solid form without at any time appearing in the liquid state. Also applied to the conversion of solid to vapor without the later return to solid state, and to a conversion directly from the vapor phase to the solid state.

5.11 Surrogate standard - A surrogate standard is a chemically inert compound (not expected to occur in the environmental sample) which is added to each sample, blank and matrix spiked sample before extraction and analysis. The recovery of the surrogate standard is used to monitor unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within acceptable limits.

5.12 Retention time window - Retention time window is determined for each analyte of interest and is the time from injection to elution of a specific chemical from a chromatographic column. The window is determined by three injections of a single component standard over a 72-hr period as plus or minus three times the standard deviation of the absolute retention time for that analyte.

6. Interferences

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that result in discrete artifacts and/or elevated baselines in the detector profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

6.1.1 Glassware must be scrupulously cleaned (33). Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinsing with tap water and reagent water. It should then be drained dry, solvent rinsed with acetone and spectrographic grade hexane. After drying and rinsing, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Glassware should be stored inverted or capped with aluminum foil.

6.1.2 The use of high purity water, reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

6.1.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. Additional clean-up by column chromatography may be required (see Section 12.4).

6.2 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although GC and HPLC conditions described allow for unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere. The use of column chromatography for sample clean-up prior to GC or HPLC analysis will eliminate most

of these interferences. The analytical system must, however, be routinely demonstrated to be free of internal contaminants such as contaminated solvents, glassware, or other reagents which may lead to method interferences. A laboratory reagent blank is run for each batch of reagents used to determine if reagents are contaminant-free.

6.3 Although HPLC separations have been improved by recent advances in column technology and instrumentation, problems may occur with baseline noise, baseline drift, peak resolution and changes in sensitivity. Problems affecting overall system performance can arise (34). The user is encouraged to develop a standard operating procedure (SOP) manual specific for his laboratory to minimize problems affecting overall system performance.

6.4 Concern during sample transport and analysis is mentioned. Heat, ozone, NO_2 and ultraviolet (UV) light may cause sample degradation. These problems should be addressed as part of the user prepared standard operating procedure manual. Where possible, incandescent or UV-shield fluorescent lighting should be used during analysis.

7. Safety

7.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the analyst (35-37).

7.2 Benzo[a]pyrene has been tentatively classified as a known or suspected, human or mammalian carcinogen. Many of the other PAHs have been classified as carcinogens. Care must be exercised when

working with these substances. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. The user should be thoroughly familiar with the chemical and physical properties of targeted substances (Table 1.0 and Figure 1.0).

7.3 Treat all selective polynuclear aromatic hydrocarbons as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste and should be disposed according to regulations. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination.

7.4 Because the sampling configuration (filter and backup adsorbent) has demonstrated greater than 95% collection efficiency for targeted PAHs, no field recovery evaluation will occur as part of this procedure.

8. Apparatus

8.1 Sample Collection

8.1.1 General Metal Works (GMW) Model PS-1 Sampler, or equivalent [General Metal Works, Inc., 145 South Miami Ave., Village of Cleves, Ohio, 45002, (800-543-7412)].

8.1.2 At least two Model PS-1 sample cartridges and filters assembled for PS-1 sampler.

8.1.3 GMW Model PS-1 calibrator and associated equipment - General Metal Works, Inc., Model GMW-40, 145 South Miami Ave., Village of Cleves, Ohio, 45002, (800-543-7412).

8.1.4 Ice chest - to store samples at 0°C after collection.

8.1.5 Data sheets for each sample for recording the location and sample time, duration of sample, starting time, and volume of air sampled.

8.1.6 Airtight, labeled screw-capped container sample cartridges (wide mouth, preferrably glass with Teflon seal or other non-contaminating seals) to hold filter and adsorbent cartridge during transport to analytical laboratory.

8.1.7 Portable Tripod Sampler (optional) - user prepared (38).

8.2 Sample Clean-up and Concentration

8.2.1 Soxhlet extractors capable of extracting GMW Model PS-1 filter and adsorbent cartridges (2.3" x 5" length), 500 mL flask, and condenser.

8.2.2 Pyrex glass tube furnace system for activating silica gel at 180°C under purified nitrogen gas purge for an hour, with capability of raising temperature gradually.

8.2.3 Glass vial, 40 mL.

8.2.4 Erlenmeyer flask, 50 mL - best source. [Note: Reuse of glassware should be minimized to avoid the risk of cross-contamination. All glassware that is used, especially glassware that is reused, must be scrupulously cleaned as soon as possible after use. Rinse glassware with the last solvent used in it and then with high-purity acetone and hexane. Wash with hot water containing detergent. Rinse with copious amount of tap water and several portions of distilled water. Drain, dry, and heat a muffle furnace at 400°C for 2 to 4 hours. Volumetric glassware must not be heated in a muffle furnace; rather, it should be rinsed with high-purity acetone and hexane. After the glassware is dry and cool, rinse it with hexane, and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.]

8.2.5 Polyester gloves for handling cartridges and filters.

8.2.6 Minivials - 2 mL, borosilicate glass, with conical reservoir and screw caps lines with Teflon-faced silicone disks, and a vial holder.

8.2.7 Stainless steel Teflon® coated spatulas and spoons.

8.2.8 Kuderna-Danish (KD) apparatus - 500 mL evaporation flask (Kontes K-570001-500 or equivalent), 10 mL graduated concentrator tubes (Knotes K-570050-1025 or equivalent) with ground-glass stoppers, and 3-ball macro Snyder Column (Kontes K-5700010500, K-50300-0121, and K-569001-219, or equivalent).

8.2.9 Adsorption columns for column chromatography - 1-cm x 10-cm with stands.

8.2.10 Glove box for working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents, reagents, etc.

8.2.11 Vacuum Oven - Vacuum drying oven system capable of maintaining a vacuum at 240 torr (flushed with nitrogen) overnight.

8.2.12 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate - best source.

8.2.13 Laboratory refrigerator with chambers operating at 0°C and 4°C.

8.2.14 Boiling chips - solvent extracted, 10/40 mesh silicon carbide or equivalent.

8.2.15 Water bath - heated, with concentric ring cover, capable of temperature control (± 5°C).

8.2.16 Vortex evaporator (optional).

8.3 Sample Analysis

8.3.1 Gas Chromatography with Flame Ionization Detection (FID).

8.3.1.1 Gas chromatography: Analytical system complete with gas chromatography suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

8.3.1.2 Packed Column: 1.8-m x 2-mm I.D. glass column packed with 3% OV-17 on Chromosorb W-AW-DMCS (100/120 mesh) or equivalent (Supelco Inc., Supelco Park, Bellefonte, Pa. Supelco SPB-5).

8.3.1.3 Capillary Column: 30-m x 0.25-mm ID fused silica column coated with 0.25 u thickness 5% phenyl, 90% methyl siloxane (Supelco Inc., Supelco Park, Bellefonte, Pa.).

8.3.1.4 Detector: Flame Ionization (FI)

8.3.2 Gas Chromatograph with Mass Spectroscopy Detection Coupled with Data Processing System (GC/MS/DS).

8.3.2.1 The GC must be equipped for temperature programming, and all required accessories must be available, including syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column injection techniques can be used but they may severely reduce column lifetime for nonchemically bonded columns. In this protocol, a 1-3 uL injection volume is used consistently. With some GC injection ports, however, 1 uL injections may produce some improvement in precision and chromatographic

separation. A 1 uL injection volume may be used if adequate sensitivity and precision can be achieved. [NOTE: If 1 uL is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1 uL.]

8.3.2.2 Gas Chromatograph-Mass Spectrometer Interface. The gas chromatograph is usually coupled directly to the mass spectrometer source. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless steel. The interface components should be compatible with 320°C temperatures. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the MS source. Graphic ferrules should be avoided in the GC injection area since they may adsorb PAHs. Vespel® or equivalent ferrules are recommended.

8.3.2.3 Mass Spectrometer. The static resolution of the instrument must be maintained at a minimum of 10,000 (10 percent valley). The mass spectrometer should be operated in the selected ion mode (SIM) with a total cycle time (including voltage reset time) of one second or less (Section 14.2).

8.3.2.4 Mass spectrometer: Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria (Section 14.5.1).

8.3.2.5 Data System. A dedicated computer data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and multi-ion detector (MID) traces (displays of intensities of each m/z being monitored

as a function of time) must be acquired during the analyses. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The detector zero setting must allow peak-to-peak measurement of the noise on the baseline.

8.3.2.6 GC Column. A fused silica column (50-m x 0.25-mm I.D.) HP Ultra #2 crosslinked 5% phenyl methylsilicone, 0.25 um film thickness (Hewlett-Packard Co., Crystal Lake, IL) is utilized to separate individual PAHs. Other columns may be used for determination of PAHs. Minimum acceptance criteria must be determined as per Section 14.2. At the beginning of each 12-hour period (after mass resolution has been demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples.

8.3.2.7 Balance - Mettler balance or equivalent.

8.3.2.8 All required syringes, gases, and other pertinent supplies to operate the GC/MS system.

8.3.2.9 Pipettes, micropipettes, syringes, burets, etc., to make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25 uL and 100 uL.

8.3.3 High Performance Liquid Chromatography (HPLC) System.

8.3.3.1 Gradient HPLC system - Consisting of acetonitrile and water phase reservoirs; mixing chamber; a high pressure pump; an injection valve (automatic sampler with an optional 25 uL loop injector); a Vydac C-18 bonded phase reverse phase (RP) column, (The Separations Group, P.O. Box 867, Hesperia, CA 92345) or equivalent (25-cm x 4.6-mm ID); a variable wavelength UV/Fluorescence detector and a data system or strip chart recorder. A Spectra Physics 8100 liquid chromatograph multi-microprocessor controlled, with ternary gradient pumping system, constant flow, autosampler injector (10 uL injection loop), and column oven (optional).

8.3.3.2 Guard column - 5-cm guard column pack with Vydac reverse phase C-18 material.

8.3.3.3 Reverse phase analytical column - Vydac or equivalent, C-18 bonded phase RP column (The Separation Group, P.O. Box 867, Hesperia, Ca., 92345), 4.6-mm x 25-cm, 5-micron particle diameter.

8.3.3.4 LS-4 fluorescence spectrometer, Perkin Elmer, separate excitation and emission, monochromator positioned by separate microprocessor-controlled flow cell and wavelength programming ability (optional).

8.3.3.5 Ultraviolet/visible detector, Spectra Physics 8440, deuterium Lamp, capable of programmable wavelengths (optional).

8.3.3.6 Dual channel Spectra Physics 4200 Computing Integrator, measures peak areas and retention times from recorded chromatographs. IBM PC XT will Spectra Physics Labnet system for data collection and storage (optional).

9. Reagents and Materials

9.1 Sample Collection

9.1.1 Acid-washed quartz fiber filter - 105 mm micro quartz fiber binderless filter (General Metal Works, Inc., Cat. No. GMW QMA-4, 145 South Miami Ave., Village of Cleves, Ohio, 45002 [800-543-7412] or Supelco Inc., Cat. No. 1-62, Supelco Park, Bellefonte, PA, 16823-0048).

9.1.2 Polyurethane foam (PUF) - 3 inch thick sheet stock, polyether type (density 0.022 g/cm^3) used in furniture upholstering (General Metal Works, Inc., Cat. No. PS-1-16, 145 South Miami Ave., Village of Cleves, Ohio, 45002 [800-543-7412] or Supelco Inc., Cat. No. 1-63, Supelco Park, Bellefonte, PA, 16823-0048).

9.1.3 XAD-2 resin - Supelco Inc., Cat. No. 2-02-79, Supelco Park, Bellefonte, PA, 16823-0048.

9.1.4 Hexane-rinsed aluminum foil - best source.

9.1.5 Hexane-reagent grade, best source.

9.2 Sample Clean-up and Concentration

9.2.1 Soxhlet Extraction

9.2.1.1 Methylene chloride - chromatographic grade, glass-distilled, best source.

9.2.1.2 Sodium sulfate, anhydrous - (ACS) granular anhydrous (purified by washing with methylene chloride followed by heating at 400°C for 4 hrs in a shallow tray).

9.2.1.3 Boiling chips - solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

9.2.1.4 Nitrogen - high purity grade, best source.

9.2.1.5 Ether - chromatographic grade, glass-distilled, best source.

9.2.1.6 Hexane - chromatographic grade, glass-distilled, best source.

9.2.1.7 Dibromobiphenyl - chromatographic grade, best source. Used for internal standard.

9.2.1.8 Decafluorobiphenyl - chromatographic grade, best source. Used for internal standard.

9.2.2 Solvent Exchange

9.2.2.1 Cyclohexane - chromatographic grade, glass-distilled, best source.

9.2.3 Column Clean-up

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9.2.3.1 Silica gel - high purity grade, type 60, 70-230 mesh; extracted in a Soxhlet apparatus with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activated by heating in a foil-covered glass container for 24 hours at 130°C.

9.2.3.2 Sodium sulfate, anhydrous - (ACS) granular anhydrous (See Section 9.2.1.2).

9.2.3.3 Pentane - chromatographic grade, glass-distilled, best source.

Lobar Prepacked Column

9.2.3.4 Silica gel lobar prepacked column - E. Merck, Darmstadt, Germany [Size A(240-10) Lichroprep Si (40-63 um)].

9.2.3.5 Precolumn containing sodium sulfate - American Chemical Society (ACS) granular anhydrous (purified by washing with methylene chloride followed by heating at 400°C for 4 hours in a shallow tray).

9.2.3.6 Hexane - chromatographic grade, glass-distilled, best source.

9.2.3.7 Methylene chloride - chromatographic grade, glass-distilled, best source

9.2.3.8 Methanol - chromatographic grade, glass-distilled, best source.

9.3 Sample Analysis

9.3.1 Gas Chromatography Detection

9.3.1.1 Gas cylinders of hydrogen and helium - ultra high purity, best source.

9.3.1.2 Combustion air - ultra high purity, best source.

9.3.1.3 Zero air - Zero air may be obtained from a cylinder or zero-grade compressed air scrubbed with Drierite® or silica gel and 5A molecular sieve or activated charcoal, or by catalytic cleanup of ambient air. All zero air should be passed through a liquid argon cold trap for final cleanup.

9.3.1.4 Chromatographic-grade stainless steel tubing and stainless steel plumbing fittings - for interconnections. [Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL, 60015, (312) 948-8600]. [Note: All such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.]

9.3.1.5 Native and isotopically labeled PAHs isomers for calibration and spiking standards-[Cambridge Isotopes, 20 Commerce Way, Woburn, MA, 01801 (617-547-1818)]. Suggested isotopically labeled PAH isomers are:

- o perylene - d_{12}
- o chrysene - d_{12}
- o acenaphthene - d_{10}
- o naphthalene - d_8
- o phenanthrene - d_{10}

9.3.1.6 Decafluorotriphenylphosphine (DFTPP) - best source, used for tuning GC/MS.

9.3.2 High Performance Liquid Chromatography Detection

9.3.2.1 Acetonitrile - chromatographic grade, glass-distilled, best source.

9.3.2.2 Boiling chips - solvent extracted, approximatley 10/40 mesh (silicon carbide or equivalent).

9.3.2.3 Water - HPLC Grade. Water must not have an interference that is observed at the minimum detectable limit (MDL) of each parameter of interest.

9.3.2.4 Decafluorobiphenyl - HPLC grade, best source (used for internal standard).

10. Preparation of Sample Filter and Adsorbent

10.1 Sampling Head Configuration

10.1.1 The sampling head (Figure 2) consist of a filter holder compartment followed by a glass cartridge for retaining the adsorbent.

10.1.2 Before field use, both the filter and adsorbent must be cleaned to <10 ng/apparatus of B[a]P or other PAHs.

10.2 Glass Fiber Filter Preparation

10.2.1 The glass fiber filters are baked at 600°C for five hours before use. To insure acceptable filters, they are extracted with methylene chloride in a Soxhlet apparatus, similar to the cleaning of the XAD-2 resin (see Section 10.3).

10.2.2 The extract is concentrated and analyzed by either GC or HPLC. A filter blank of <10 ng/filter of B[a]P or other PAHs is considered acceptable for field use.

10.3. XAD-2 Adsorbent Preparation

10.3.1 For initial cleanup of the XAD-2, a batch of XAD-2 (approximately 60 grams) is placed in a Soxhlet apparatus [see Figure 3(a)] and extracted with methylene chloride for 16 hours at approximately 4 cycles per hour.

10.3.2 At the end of the initial Soxhlet extraction, the spent methylene chloride is discarded and replaced with fresh reagent. The XAD-2 resin is once again extracted for 16 hours at approximately 4 cycles per hour.

10.3.3 The XAD-2 resin is removed from the Soxhlet apparatus, places in a vacuum oven connected to an ultra-purge nitrogen gas stream and dries at room temperature for approximately 2-4 hours (until no solvent odor is detected).

10.3.4 A nickel screen (mesh size 200/200) is fitted to the bottom of a hexane-rinsed glass cartridge to retain the XAD-2 resin.

10.3.5 The Soxhlet extracted/vacuum dried XAD-2 resin is placed into the sampling cartridge (using polyester gloves) to a depth of approximately 2 inches. This should require approximately 55 grams of adsorbent.

10.3.6 The glass module containing the XAD-2 adsorbent is wrapped with hexane-rinsed aluminum foil, placed in a labeled container and tightly sealed with Teflon® tape.

10.3.7 At least one assemble cartridge from each batch must be analyzed, as a laboratory blank, using the procedures described in Section 13, before the batch is considered acceptable for field use. A blank of <10 ng/cartridge of B[a]P on other PNA's is considered acceptable.

10.4 PUF Sampling Cartridge Preparation

10.4.1 The PUF adsorbent is a polyether-type polyurethane foam (density No. 3014 or 0.0225 g/cm^3) used for furniture upholstery.

10.4.2 The PUF inserts are 6.0-cm diameter cylindrical plugs cut from 3-inch sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (see Figure 1). During cutting, the die is rotated at high speed (e.g., in a drill press) and continuously lubricated with water.

10.4.3 For initial cleanup, the PUF plug is placed in a Soxhlet apparatus [see Figure 3(a)] and extracted with acetone for 14-24 hours at approximately 4 cycles per hour. [Note: When cartridges are reused, 5% diethyl ether in n-hexane can be used as the cleanup solvent.]

10.4.4 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).

10.4.5 The PUF is placed into the glass sampling cartridge using polyester gloves. The module is wrapped with hexane-rinsed aluminum foil, placed in a labeled container, and tightly sealed.

10.4.6 At least one assembled cartridge from each batch must be analyzed, as a laboratory blank, using the procedures described in Section 13, before the batch is considered acceptable for field use. A blank level of <10 ng/plug for single compounds is considered to be acceptable.

11. Sample Collection

11.1 Description of Sampling Apparatus

11.1.1 The entire sampling system can be a modification of a traditional high volume sampler (see Figure 4) or a portable sampler (see Figure 5). A unit specifically designed for this method is commercially available (Model PS-1 - General Metal Works, Inc., Village of Cleves, Ohio).

11.1.2 The sampling module consists of a glass sampling cartridge and an air-tight metal cartridge holder, as outlined in Section 10.1. The adsorbent (XAD-2 or PUF) is retained in the glass sampling cartridge.

11.2 Calibration of Sampling System

Each sampler is to be calibrated: 1) when new; 2) after major repairs or maintenance; 3) whenever any audit point deviates from the calibration curve by more than 7%; 4) when a different sample collection media, other than that which the sampler was originally calibrated to, will be used for sampling; or 5) at the frequency specified in the user Standard Operating Procedure (SOP) manual in which the samplers are utilized.

11.2.1 Calibration of Flow Rate Transfer Standard

Calibration of the modified high volume air sampler in the field is performed using a calibrated orifice flow rate transfer standard. The flow rate transfer standard must be certified in the laboratory against a positive displacement rootsmeter (see Figure 6). Once certified, the recertification is performed rather infrequently if the orifice is protected from damage. Recertification of the orifice flow rate transfer standard is performed once per year utilizing a set of five (5) multihole resistance plates. [Note: The 5 multihole resistance plates are used to change the flow through the orifice so that several points can be obtained for the orifice calibration curve.]

11.2.1.1 Record the room temperature (t_l in °C) and barometric pressure (P_b in mm Hg) on Orifice Calibration Data Sheet (see Figure 7). Calculate the room temperature in °K (absolute temperature) and record on Orifice Calibration Data Sheet.

$$t_l \text{ in K} = 273° + t_l \text{ in °C}$$

11.2.1.2 Set up laboratory orifice calibration equipment as illustrated in Figure 6. Check the oil level of the rootsmeter prior to starting. There are three oil level indicators, one at the clear plastic end, and two sight glasses, one at each end of the measuring chamber.

11.2.1.3 Check for leaks by clamping both manometer lines blocking the orifice with cellophane tape, turning on the high volume motor, and noting any change in the rootsmeter's reading. If the rootsmeter's reading changes, then there is a leak in the system or in the tape. Eliminate the leak before proceeding. If the rootsmeter's reading remains constant, turn off the hi-vol motor, remove the cellophane tape, and unclamp both manometer lines.

11.2.1.4 Install the 5-hole resistance plate between the orifice and the filter adapter.

11.2.1.5 Turn manometer tubing connectors one turn counterclockwise. Make sure all connectors are open.

11.2.1.6 Adjust both manometer midpoints by sliding their movable scales until the zero point corresponds with the bottom of the meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required for the water manometer, remove tubing connector and add clean water).

11.2.1.7 Turn on the hi-vol motor and let it run for five minutes to set the motor brushes.

11.2.1.8 Record both manometer readings-orifice water manometer (ΔH) and rootsmeter mercury manometer (ΔP). [Note: ΔH is the sum of the difference from zero (0) of the two column heights.]

11.2.1.9 Record the time, in minutes, required to pass a known volume of air (approximately 200-300 ft^3 of air for each resistance plate) through the rootsmeter by using the rootsmeter's digital volume dial and a stopwatch.

11.2.1.10 Turn off the high volume motor.

11.2.1.11 Replace the 5-hole resistance plate with the 7-hole resistance plate.

11.2.1.12 Repeat Sections 11.2.1.3 through 11.2.1.10.

11.2.1.13 Repeat for each resistance plate. Note results on Orifice Calibration Data Sheet (see Figure 7). Only a minute is needed for warm-up of the motor. Be sure to tighten the orifice enough to eliminate any leaks. Also check the gaskets for cracks. [Note: The placement of the orifice prior to the rootsmeter causes the pressure at the inlet of the rootsmeter to be reduced below atmospheric conditions, thus causing the measured volume to be incorrect. The volume measured by the rootsmeter must be corrected.]

11.2.1.14 Correct the measured volumes with the following formula and record the standard volume on the Orifice Calibration Data Sheet:

$$V_{std} = V_m \frac{P_1 - \Delta P}{P_{std}} \frac{T_{std}}{T_1}$$

where: V_{std} = standard volume (std m^3).
V_m = actual volume measured by the rootsmeter (m^3).
P_1 = barometric pressure during calibration (mm Hg).
ΔP = differential pressure at inlet to volume meter (mm Hg).
P_{std} = 760 mm Hg.
T_{std} = 298 K.
T_1 = ambient temperature during calibration (K).

11.2.1.15 Record standard volume on Orifice Calibration Data Sheet.

11.2.1.16 The standard flow rate as measured by the rootsmeter can now be calculated using the following formula:

$$Q_{std} = \frac{V_{std}}{\theta}$$

where: Q_{std} = standard volumetric flow rate, std m3/min.
θ = elapsed time, min.

11.2.1.17 Record the standard flow rates to the nearest 0.01 std m^3/min.

11.2.1.18 Calculate and record $\sqrt{\Delta H(P_1/P_{std})\ (298/T_1)}$ value for each standard flow rate.

11.2.1.19 Plot each $\sqrt{\Delta H(P_1/P_{std})\ (298/T_1)}$ value (y-axis) versus its associated standard flow rate (x-axis) on arithmetic graph paper, draw a line of best fit between the individual plotted points and calculate the linear regression slope (M) and intercept (b).

11.2.1.20 Commercially available calibrator kits are available [General Metal Works Inc., Model GMW-40, 145 South Miami Avenue, Village of Cleves, Ohio, 45002 (1-800-543-7412)].

11.2.2 Calibration of The High Volume Sampling System Utilizing Calibrated Multi-point Flow Rate Transfer Standard

11.2.2.1 The airflow through the sampling system can be monitored by a venturi/magnehelic assembly, as illustrated in Figure 4 or by a u-tube assembly connected to the high volume portable design as illustrated in Figure 5. The field sampling system must be audited every six months using a flow rate transfer standard, as described in the U.S. EPA High Volume Sampling Method, 40 CFR 50, Appendix B. A single-point calibration must be performed before and after each sample collection, using a transfer standard calibrated as described in Section 11.2.1.

11.2.2.2 Prior to initial multi-point calibration, a "dummy" adsorbent cartridge and filter are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow rate corresponding to 110% of the desired flow rate (typically 0.20 - 0.28 m^3/min) is indicated on the Magnehelic gauge (based on the previously obtained multi-point calibration curve). The

motor is allowed to warm up for 10 minutes and then the flow control valve is adjusted to achieve the desired flow rate. Turn off the sampler. The ambient temperature and barometric pressure should be recorded on the Field Calibration Data Sheet (Figure 9).

11.2.2.3 The flow rate transfer standard is placed on the sampling head, and a manometer is connected to the tap on the transfer standard using a length of tubing. Properly align the retaining rings with filter holder and secure by tightening the three screw clamps. Set the zero level of the manometer. Attach the magnehelic gage to the sampler venturi quick release connections. Adjust the zero (if needed) using the zero adjust screw on the face of the gage.

11.2.2.4 Turn the flow control valve to the fully open position and turn the sampler on. Adjust the flow control valve until a magnehelic reading of approximately 70 in. is obtained. Allow the magnehelic and manometer readings to stabilize and record these values.

11.2.2.5 Adjust the flow control valve and repeat until six or seven uniformally spaced magnehelic readings are recorded spanning the range of approximately 40-70 in. Record the readings on the Field Calibration Data Sheet (see Figure 9). [Note: Use of some filter/sorbent media combinations may restrict the airflow resulting in a maximum magnehelic reading of 60 in. or less. In such cases, a variable transformer should be placed in-line between the 110 volt power source and the sampler so that the line voltage can be increased sufficiently to obtain a maximum magnehelic reading approaching 70 in.].

11.2.2.6 Adjust the orifice manometer reading for standard temperature and pressure using the following equation:

$$X = \sqrt{\Delta H \frac{P_a}{P_{std}} \frac{T_{std}}{T_a}}$$

where: X = adjusted manometer reading to standard temperature and pressure (in. water).

ΔH = observed manometer reading (in water).

P_a = current barometric pressure (mm Hg).

P_{std} = 760 mm Hg.

T_a = current temperature (K), (K = °C + 273).

T_{std} = standard temperature (298 K).

11.2.2.7 Calculate the standard flow rate for each corrected manometer reading by the following equation:

$$Q_{std} = \frac{X - b}{M}$$

where:

Q_{std} = standard flow rate (m^3/min).

M = slope of flow rate transfer standard calibration curve.

X = corrected manometer reading from 11.2.2.6 (in water).

b = intercept of flow rate transfer standard calibration curve.

11.2.2.8 Adjust the magnehelic gage readings to standard temperature and pressure using the following equation:

$$M_{std} = \sqrt{\frac{(M)(P_a)}{P_{std}} \quad \frac{T_{std}}{T_a}}$$

where:

M_{std} = adjusted magnehelic reading to standard temperature and pressure (inches of water).

M = observed magnehelic reading (inches of water).

P_a = ambient atmospheric pressure (mm Hg).

P_{std} = standard pressure (760 mm Hg).

T_a = ambient temperature (K), (K = °C + 273).

T_{std} = standard temperature (298 K).

11.2.2.9 Plot each M_{std} value (y-axis) versus its associated Q_{std} standard (x-axis) on arithmetic graph paper. Draw a line of best fit between the individual plotted points. This is the calibration curve for the venturi. Retain with sampler.

11.2.2.10 Record the corresponding Q_{std} for each M_{std} under Q_{std} column on Field Calibration Data Sheet, Figure 9.

11.2.3 Single-point Audit of The High Volume Sampling System Utilizing Calibrated Flow Rate Transfer Standard

11.2.3.1 A single point flow audit check is performed before and after each sampling period utilizing the Calibration Flow Rate Transfer Standard (Section 11.2.1).

11.2.3.2 Prior to single point audit, a "dummy" adsorbent cartridge and filter are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a

sample flow rate corresponding to 110% of the desired flow rate (typically 0.20-0.28 m^3/min) is indicated on the magnehelic gauge (based on the previously obtained multi-point calibration curve). The motor is allowed to warm up for 5 minutes and then the flow control valve is adjusted to achieve the desired flow rate. Turn off the sampler. The ambient temperature and barometric pressure should be recorded on a Field Test Data Sheet (Figure 10).

11.2.3.3 The flow rate transfer standard is placed on the sampling head.

11.2.3.4 Properly align the retaining rings with filter holder and secure by tightening the three screw clamps.

11.2.3.5 Using tubing, attach one manometer connector to the pressure tap of the transfer standard. Leave the other connector open to the atmosphere.

11.2.3.6 Adjust the manometer midpoint by sliding the movable scale until the zero point corresponds with the water meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required, remove tubing connector and add clean water.)

11.2.3.7 Turn on high volume motor and let run for five minutes.

11.2.3.8 Record the pressure differential indicated, ΔH, in inches of water. Be sure stable ΔH has been established.

11.2.3.9 Record the observed magnehelic gauge reading, in inches of water. Be sure stable M has been established.

11.2.3.10 Using previously established Flow Rate Transfer Standard curve, calculate Q_{std} (see steps 11.2.2.6 - 11.2.2.7).

11.2.3.11 Using previously established venturi calibration curve, calculate the indicated Q_{std} (Section 11.2.2.9).

11.2.3.12 A multi-point calibration of the Flow Rate Transfer Standard against a primary standard, must be obtained annually, as outlined in Section 11.2.1.

11.2.3.13 Remove Flow Rate Transfer Standard and dummy adsorbent cartridge and filter assembly.

11.3 Sample Collection

11.3.1 After the sampling system has been assembled and flow checked as described in Sections 11.1 and 11.2, it can be used to collect air samples, as described in Section 11.3.2.

11.3.2 The samples should be located in an unobstructed area, at least two meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sample head.

11.3.3 With the empty sample module removed from the sampler, rinse all sample contact areas using reagent grade hexane in a Teflon® squeeze bottle. Allow the hexane to evaporate from the module before loading the samples.

11.3.4 Detach the lower chamber of the rinsed sampling module. While wearing disposable clean lint-free nylon or powder-free surgical gloves, remove a clean glass cartridge/sorbent from its container (wide mouthed glass jar with a Teflon®-lined lid) and unwrap its aluminum foil covering. The foil should be replaced back in the sample container to be re-used after the sample has been collected.

11.3.5 Insert the cartridge into the lower chamber and tightly reattach it to the module.

11.3.6 Using clean Teflon® tipped forceps, carefully place a clean fiber filter atop the filter holder and secure in place by clamping the filter holder ring over the filter using the three screw clamps. Insure that all module connections are tightly assembled. [Note: Failure to do so

could result in air flow leaks at poorly sealed locations which could affect sample representativeness]. Ideally, sample module loading and unloading should be conducted in a controlled environment or at least a centralized sample processing area so that the sample handling variables can be minimized.

11.3.7 With the module removed from the sampler and the flow control valve fully open, turn the pump on and allow it to warm-up for approximately 5 minutes.

11.3.8 Attach a "dummy" sampling module loaded with the exact same type of filter and sorbent media as that which will be used for sample collection.

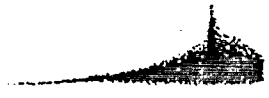
11.3.9 With the sampler off, attach the Magnahelic gage to the sampler. Turn the sampler on and adjust the flow control valve to the desired flow (normally as indicated by the cfm) magnahelic gauge reading and reference by the calibration chart. [Note: Breakthrough has not been a problem for all PAHs outlined in Section 1.5 using this sampling method except anthracene and penanthrene]. Once the flow is properly adjusted, extreme care should be taken not to inadvertantly alter its setting.

11.3.10 Turn the smpler off and remove both the "dummy" module and the Magnahelic gauge. The sampler is now ready for field use.

11.3.11 The zero reading of the sampler Magnehelic is checked. Ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and adsorbent sample number are recorded on the Field Test Data Sheet (see Figure 10). Attach the loaded sampler module to the sampler.

11.3.12 The voltage variator and flow control valve are placed at the settings used in Section 11.2.2, and the power switch is turned on. The elapsed time meter is activated and the start time is recorded. The flow (Magnehelic setting) is adjusted, if necessary, using the flow control valve.

11.3.13 The Magnehelic reading is recorded every six hours during the sampling period. The calibration curve



(Section 11.2.4) is used to calculate the flow rate. Ambient temperature, barometric pressure, and Magnehelic reading are recorded at the beginning and end of the sampling period.

11.3.14 At the end of the desired sampling period, the power is turned off. Carefully remove the sampling head containing the filter and adsorbent cartridge to a clean area.

11.3.15 While wearing disposable lint free nylon or surgical gloves, remove the sorbent cartridge from the lower module chamber and lay it on the retained aluminum foil in which the sample was originally wrapped.

11.3.16 Carefully remove the glass fiber filter from the upper chamber using clean Teflon® tiped forceps.

11.3.17 Fold the filter in half twice (sample side inward) and place it in the glass cartridge atop the sorbent.

11.3.18 Wrap the combined samples in aluminum foil and place them in their original glass sample container. A sample label should be completed and affixed to the sample container. Chain-of-custody should be maintained for all samples.

11.3.19 The glass containers should be stored in ice and protected from light to prevent possible photo-decomposition of collected analytes. If the time span between sample collection and laboratory analysis is to exceed 24 hours, sample must be kept refrigerated. [Note: Recent studies (13,16) have indicated that PUF does not retain, during storage, B[a]P as effectively as XAD-2. Therefore, sample holding time should not exceed 20 days.]

11.3.20 A final calculated sample flow check is performed using the calibration orifice, as described in Section 11.2.2. If calibration deviates by more than 10% from the initial reading, the flow data for that sample must be marked as suspect and the sampler should be inspected and/or removed from service.

11.3.21 At least one field filter/adsorbent blank will be returned to the laboratory with each group of samples. A field blank is treated exactly as a sample except that no air is drawn through the filter/adsorbent cartridge assembly.

11.3.22 Samples are stored at 0°C in an ice chest until receipt at the analytical laboratory, after which they are refrigerated at 4°C.

12. Sample Clean-up and Concentration

[Note: The following sample extraction, concentration, solvent exchange and analysis procedures are outlined for user convenience in Figure 11.]

12.1 Sample Identification

12.1.1 The samples are returned in the ice chest to the laboratory in the glass sample container containing the filter and adsorbent.

12.1.2 The samples are logged in the laboratory logbook according to sample location, filter and adsorbent cartridge number identification and total air volume sampled (uncorrected).

12.1.3 If the time span between sample registration and analysis is greater than 24-hrs., then the samples must be kept refrigerated. Minimize exposure of samples to fluorescence light. All samples should be extracted within one week after sampling.

12.2 Soxhlet Extraction and Concentration

12.2.1 Assemble the Soxhlet apparatus [see Figure 3(a)]. Immediately before use, charge the Soxhlet apparatus with 200 to 250 mL of methylene chloride and reflux for 2 hours. Let the apparatus cool, disassemble it, transfer the methylene chloride to a clean glass container, and retain it as a blank for later analysis, if required. Place the adsorbent and filter together in the Soxhlet apparatus (the use of an extraction thimble is optional) if using XAD-2 adsorbent in the sampling module. [Note: The filter and adsorbent are analyzed together in order to reach detection limits, avoid questionable interpretation of the data, and minimize cost.] Since methylene chloride is not a suitable solvent for PUF, 10% ether in hexane is employed to extract the PAHs from the PUF resin bed separate from the methylene chloride extraction of the accompanying filter rather than methylene chloride for the extraction of the XAD-2 cartridge.

12.2.1.1 Prior to extraction, add a surrogate standard to the Soxhlet solvent. A surrogate standard (i.e., a chemically inert compound not expected to

occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits. The following surrogate standards have been successfully utilized in determining matrix effects, sample process errors, etc. utilizing GC/FID, GC/MS or HPLC analysis.

Surrogate Standard	Concentration	Analytical Technique
Dibromobiphenyl	50 ng/uL	GC/FID
Dibromobiphenyl	50 ng/uL	GC/MS
Deuterated Standards	50 ng/uL	GC/MS
Decafluorobiphenyl	50 ng/uL	HPLC

[Note: The deuterated standards will be added in Section 14.3.2. Deuterated analogs of selective PAHs cannot be used as surrogates for HPLC analysis due to coelution problems.] Add the surrogate standard to the Soxhlet solvent.

12.2.1.2 For the XAD-2 and filter extracted together, add 300 mL of methylene chlorine to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

12.2.1.3 For the PUF extraction separate from the filter, add 300 mL of 10 percent ether in hexane to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

12.2.1.4 For the filter extraction, add 300 mL of methylene chloride to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

12.2.2 Dry the extract from the Soxhlet extraction by passing it through a drying column containing about 10 grams of anhydrous sodium sulfate. Collect the dried extract in a Kuderna-Danish (K-D) concentrator assembly. Wash the

extractor flask and sodium sulfate column with 100 - 125 mL of methylene chloride to complete the quantitative transfer.

12.2.3 Assemble a Kuderna-Danish concentrator [see Figure 3(b)] by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. [Note: Other concentration devices (vortex evaporator) or techniques may be used in place of the K-D as long as qualitative and quantitative recovery can be demonstrated.]

12.2.4 Add two boiling chips, attach a three-ball macro-Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65°C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in one hour. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an approximate volume of 5 mL, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 minutes while cooling.

12.2.5 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 5 mL of cyclohexane.

12.3 Solvent Exchange

12.3.1 Replace the K-D apparatus equipped with a Snyder column back on the water bath.

12.3.2 Increase the temperature of the hot water bath to 95-100°C. Momentarily, remove the Snyder column, add a new boiling chip, and attach a two-ball micro-Snyder column. Prewet the Snyder column, using 1 mL of cyclohexane. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers

will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

12.3.3 When the apparatus is cool, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 mL of cyclohexane. [Note: A 5 mL syringe is recommended for this operation]. Adjust the extract volume to exactly 1.0 mL with cyclohexane. Stoppe the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than 24 hours, it should be transferred to a Teflon®-sealed screw-cap vial.

12.4 Sample Cleanup By Solid Phase Exchange

Cleanup procedures may not be needed for relatively clean matrix samples. If the extract in Section 12.3.3 is clear, cleanup may not be necessary. If cleanup is not necessary, the cyclohexane extract (1 mL) can be analyzed directly by GC/FI detection, excep the initial oven temperature begins at 30°C rather than 80°C for cleanup samples (see Section 13.3), or solvent exchange to acetonitrile for HPLC analysis. If cleanup is required, the procedures are presented using either handpack silica gel column as prescribe in Method 610 (see Section 18.0, citation No. 18 and 22) or the use of a Lobar prepacked silica gel column for PAH concentration and separation. Either approach can be employed by the user.

12.4.1 Method 610 Cleanup Procedure [see Figure 3(c)]

12.4.1.1 Pack a 6-inch disposable Pasture pipette (10 mm I.D. x 7 cm length) with a piece of glass wool. Push the wool to the neck of the disposable pipette. Add 10 grams of activated silica gel in methylene chloride slurry to the disposable pipette. Gently tap the column to settle the silica gel and elute the methylene chloride. Add 1 gram of anhydrous sodium sulfate to the top of the silica gel column.

12.4.1.2 Prior to initial use, rinse the column with methylene chloride at 1 mL/min for 1 hr to

remove any trace of contaminants. Preelute the column with 40 mL of pentane. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 1 mL of the cyclohexane sample extract onto the column, using an additional 2 mL of cyclohexane to complete the transfer. Allow to elute through the column.

12.4.1.3 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue elution of the column. Discard the pentane eluate. [Note: The pentane fraction contains the aliphatic hydrocarbons collected on the filter/ adsorbent combination. If interested, this fraction may be analyzed for specific aliphatic organics.] Elute the column with 25 mL of methylene chloride/pentane (4 + 6) (V/V) and collect the eluate in a 500 mL K-D flask equipped with a 10 mL concentrator tube. [Note: This fraction contains the B[a]P and other moderately polar PAHs]. Elution of the column should be at a rate of about 2 mL/min. Concentrate the collected fraction to less than 10 mL by the K-D technique, as illustrated in Section 12.3 using pentane to rinse the walls of the glassware. The extract is now ready for HPLC or GC analysis. [Note: An additional elution through the column with 25 mL of methanol will collect highly polar oxygenated PAHs with more than one functional group. This fraction may be analyzed for specific polar PAHs. However, additional cleanup by solid phase extraction may be required to obtain both qualitative and quantitative data due to complexity of the eluant.]

12.4.2 Lobar Prepacked Column Procedure

12.4.2.1 The setup using the Lobar prepacked column consists of an injection port, septum, pump, precolumn containing sodium sulfate, Lobar prepacked column and solvent reservoir.

12.4.2.2 The column is cleaned and activated according to the following cleanup sequence:

Fraction	Solvent Composition	Volume (mL)
1	100% Hexane	20
2	80% Hexane/20% Methylene Chloride	10
3	50% Hexane/50% Methylene Chloride	10
4	100% Methylene Chloride	10
5	95% Methylene Chloride/5% Methanol	10
6	80% Methylene Chloride/20% Methanol	10

12.4.2.3 Reverse the sequence at the end of the run and run to the 100% hexane fraction in order to activate the column. Discard all fractions.

12.4.2.4 Pre-elute the column with 40 mL of hexane, which is also discharged.

12.4.2.5 Inject 1 mL of the cyclohexane sample extract, followed by 1 mL injection of blank cyclohexane.

12.4.2.6 Continue elution of the column with 20 mL of hexane, which is also discharged.

12.4.2.7 Now elute the column with 180 mL of a 40/60 mixture of methylene chloride/hexane respectively.

12.4.2.8 Collect approximately 180 mL of the 40/60 methylene chloride/hexane mixture in a K-D concentrator assembly.

12.4.2.9 Concentrate to less than 10 mL with the K-D assembly as discussed in Section 12.2.

12.4.2.10 The extract is now ready for either HPLC or GC analysis.

13. Gas Chromatography Analysis with Flame Ionization Detection

13.1 Gas chromatography (GC) is a quantitative analytical technique useful for PAH identification. This method provides the user the flexibility of column selection (packed or capillary) and detector [flame ionization (FI) or mass spectrometer (MS)] selection. The mass spectrometer provides for specific identification of B(a)P; however, with system optimization, other PAHs may be qualitatively and quantitatively detected using MS (see Section 14.0). This procedure provides for common GC separation of the PAHs with

subsequent detection by either FI or MS (see Figure 12.0). The following PAHs have been quantified by GC separation with either FI or MS detection:

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(e)pyrene	Phenanthrene
Benzo(g,h,i)perylene	Pyrene
Benzo(k)fluoranthene	

The packed column gas chromatographic method described here can not adequately resolve the following four pairs of compounds: anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)fluoranthene; and dibenzo(a,h) anthracene and indeno(1,2,3-cd)pyrene. The use of a capillary column instead of the packed column, also described in this method, should adequately resolve these PAHs. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, either capillary gas chromatography/mass spectroscopy (Section 14.0) or high performance liquid chromatography (Section 15.0) should be used for these compounds. This section will address the use of GC/FI detection using packed or capillary columns.

13.2 To achieve maximum sensitivity with the GC/FI method, the extract must be concentrated to 1.0 mL, if not already concentrated to 1 mL. If not already concentrated to 1 mL, add a clean boiling chip to the methylene chloride extract in the concentrator tube. Attach a two-ball micro-Snyder column. Prewet the micro-Snyder column by adding about 2.0 mL of methylene chloride to the top. Place the micro K-D apparatus on a hot water bath (60 to 65°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus. Drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of methylene chloride. Adjust the final volume to 1.0 mL and stopper the concentrator tube.

13.3 Assemble and establish the following operating parameters for the GC equipped with an FI detector:

	Capillary (A)	Capillary (B)	Packed
Identification	SPB-5 fused silica capillary, 0.25 um 5% phenyl, methyl siloxane bonded	SPB-5 fused silica capillary, 0.25 um 5% phenyl, methyl siloxane bonded	Chromosorb W-AW-DMCS (100/120 mesh) coated with 3% OV-17
Dimensions	30-m x 0.25-mm ID	30-m x 0.25-mm ID	1.8-m x 2-mm ID
Carrier Gas	Helium	Helium	Nitrogen
Carrier Gas Flow Rate	28-30 cm/sec (1 cm/minute)	28-30 cm/sec (1 cm/minute)	30-40 cm/minute
Column Program	35°C for 2 min; program at 8°C/min to 280°C and hold for 12 minutes	80°C for 2 min; program at 8°C/min to 280°C and hold for 12 minutes	Hold at 100°C for 4 minutes; program at 8°C/min to 280°C and hold for 15 minutes
Detector	Flame Ionization	Flame Ionization	Flame Ionization

(A) Without column cleanup (see Section 12.4)
(B) With column cleanup (see Section 12.4.1)

13.4 Prepare and calibrate the chromatographic system using either the external standard technique (Section 13.4.1) or the internal standard technique (Section 13.4.2). Figure 13.0 outlines the following sequence involving GC calibration and retention time window determination.

13.4.1 External Standard Calibration Procedure - For each analyte of interest, including surrogate compounds for spiking, if used, prepare calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methylene chloride. [Note: All calibration standards of interest involving selected PAHs, of the same concentration, can be prepared in the same flask.]

13.4.1.1 Prepare stock standard solutions at a concentration of 100 ug/uL by dissolving 0.100 gram of assayed PAH material in methylene chloride and diluting to vol- in a 10 mL volumetric flask. [Note: Larger volumes can be used at the convenience of the analyst.]

13.4.1.2 When compound purity is assayed to be 98% or greater, the weight can be used without correction to calculate the concentration of the stock standard. [Note: Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.] Transfer the stock standard solutions into Teflon®-sealed screw-cap bottles.

13.4.1.3 Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Stock standard solutions must be replaced after one year, or sooner, if comparison with check standards indicates a problem.

13.4.1.4 Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with methylene chloride. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. [Note: Calibration solutions must be replaced after six months, or sooner, if comparison with a check standard indicates a problem.]

13.4.1.5 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 1- to 3-uL injections). [Note: The same amount must be injected each time.]

13.4.1.6 Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each analyte. [Note: Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount

injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration by the following equation:

$$\text{Calibration factor (CF)} = \frac{\text{Total Area of Peak}}{\text{Mass injected (in nanograms)}}$$

If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.]

13.4.1.7 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, a new calibration curve must be prepared for that analyte. Calculate the percent variance by the following equation:

$$\text{Percent variance} = \frac{R_2 - R_1}{R_1} \times 100$$

where

R_2 = Calibration factor from succeeding analysis.

R_1 = Calibration factor from first analysis.

13.4.2 Internal Standard Calibration Procedure - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested. [Note: It is recommended that the internal standard approach be used only when the GC/MS procedure is employed due to coeluting species.]

13.4.2.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask.

13.4.2.2 To each calibration standard, add a known constant amount of one or more internal standard and dilute to volume with methylene chloride. [Note: One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.]

13.4.2.3 Inject each calibration standard using the same introduction technique that will be applied to the actual samples (e.g., 1- to 3-uL injection).

13.4.2.4 Tabulate the peak height or area responses against the concentration of each compound and internal standard.

13.4.2.5 Calculate response factors (RF) for each compound as follows:

$$\text{Response Factor (RF)} = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the analyte to be measured (area units or peak height).

A_{is} = Response for the internal standard. (area units or peak height).

C_{is} = Concentration of the internal standard, (ug/L).

C_s = Concentration of the analyte to be measured, (ug/L).

13.4.2.6 If the RF value over the working range is constant (<20% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. [Note: Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} versus RF.]

13.4.2.7 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards.

13.4.2.8 If the response for any analyte varies from the predicted response by more than ±20%, a new calibration curve must be prepared for that compound.

13.5 Retention Time Windows Determination

13.5.1 Before analysis can be performed, the retention time windows must be established for each analyte.

13.5.2 Make sure the GC system is within optimum operating conditions.

13.5.3 Make three injections of the standard containing all compounds for retention time window determination. [Note: The retention time window must be established for each analyte throughout the course of a 72-hr period.]

13.5.4 The retention window is defined as plus or minus three times the standard deviation of the absolute retention times for each standard.

13.5.5 Calculate the standard deviation of the three absolute retention times for each single component standard. In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

13.5.6 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be noted and retained in a notebook by the laboratory as part of the user SOP and as a quality assurance check of the analytical system.

13.6 Sample Analysis

13.6.1 Inject 1- to 3-uL of the methylene chloride extract from Section 13.2 (however, the same amount each time) using the splitless injection technique when using capillary column. [Note: Smaller (1.0 uL) volumes can be injected if automatic devices are employed.]

13.6.2 Record the volume injected and the resulting peak size in area units or peak height.

13.6.3 Using either the internal or external calibration procedure, determine the identity and quantity of each component peak in the sample chromatogram through retention time window and established calibration curve. Table 2 outlines typical retention times for selected PAHs, using both the packed and capillary column technique coupled with FI detection, while Figure 14.0 illustrates typical chromatogram for a packed column analysis.

13.6.3.1 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

13.6.3.2 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte from Section 13.5.4 as the midpoint of the window for that day. The daily retention time window equals the midpoint $\pm$ three times the standard deviation determined in Section 13.5.4.

13.6.3.3 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. [Note: Confirmation may be required on a second GC column, or by GC/MS (if concentration permits) or by other recognized confirmation techniques if overlap of peaks occur.]

13.6.3.4 Validation of GC system qualitative performance is performed through the use of the midlevel standards. If the mid-level standard falls outside its daily retention time window, the system

is out of control. Determine the cause of the problem and perform a new calibration sequence (see Section 13.4).

13.6.3.5 Additional validation of the GC system performance is determined by the surrogate standard recovery. If the recovery of the surrogate standard deviates from 100% by not more than 20%, then the sample extraction, concentration, clean-up and analysis is certified. If it exceeds this value, then determine the cause of the problem and correct.

13.6.4 Determine the concentration of each analyte in the sample according to Sections 17.1 and 17.2.1.

14. Gas Chromatography with Mass Spectroscopy Detection

14.1 The analysis of the extracted sample for benzo[a]pyrene and other PAHs is accomplished by an electron impact gas chromatography/mass spectrometry (EI GC/MS) in the selected ion monitoring (SIM) mode with a total cycle time (including voltage reset time) of one second or less. The GC is equipped with an ultra No. 2 fused silica capillary column (50-m x 0.25-mm I.D.) with helium carrier gas for analyte separation. The GC column is temperature controlled and interfaced directly to the MS ion source.

14.2 The laboratory must document that the EI GC/MS system is properly maintained through periodic calibration checks. The GC/MS system should have the following specifications:

Mass range: 35-500 amu
Scan time: 1 sec/scan
GC Column: 50 m x 0.25 mm I.D. (0.25 um film thickness)
Ultra No. 2 fused silica capillary column or equivalent
Initial column temperature and hold time: 40°C for 4 min
Column temperature program: 40-270°C at 10°C/min
Final column temperature hold: 270°C (until benzo[g,h,i] perylene has eluted)
Injector temperature: 250-300°C
Transfer line temperature: 250-300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
EI Condition: 70 eV
Mass Scan: Follow manufacturer instruction for select ion monitoring (SIM) mode.
Sample volume: 1-3 uL
Carrier gas: Helium at 30 cm/sec.

The GC/MS is tuned using a 50 ng/uL solution of decafluorotriphenylphosphine (DFTPP). The DFTPP permits the user to tune the mass spectrometer on a daily basis. If properly tuned, the DFTPP key ions and ion abundance criteria should be met as outlined in Table 3.

14.3 The GC/MS operating conditions are outlined in Table 4. The GC/MS system can be calibrated using the external standard technique (Section 14.3.1) or the internal standard technique (Section 14.3.2). Figure 15.0 outlines the following sequence involving the GC/MS calibration.

14.3.1 External standard calibration procedure.

14.3.1.1 Prepare calibration standard of B[a]P or other PAHs at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methylene chloride. The stock standard solution of B[a]P (1.0 ug/uL) must be prepared from pure standard materials or purchased as certified solutions.

14.3.1.2 Place 0.0100 grams of native B[a]P or other PAHs on a tared aluminum weighing disk and weigh on a Mettler balance.

14.3.1.3 Quantitatively, transfer to a 10 ml volumetric flask. Rinse the weighing disk with several small portions of methylene chloride. Ensure all material has been transferred.

14.3.1.4 Dilute to mark with methylene chloride.

14.3.1.5 The concentration of the stock standard solution of B[a]P or other PAHs in the flask is 1.0 ug/uL [Note: Commerically prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.]

14.3.1.6 Transfer the stock standard solutions into Teflon®-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

14.3.1.7 Stock standard solutions must be replaced after 1 yr or sooner if comparison with quality control check samples indicates a problem.

14.3.1.8 Calibration standards at a minimum of five concentration levels should be prepared. [Note: One of the calibration standards should be at a concentration near, but above the method detection limit; the others should correspond to the range of concenrations found in the sample but should not exceed the working range of the GC/MS system.] Accurately pipette 1.0 ml of the stock solution (1 ug/uL) into another 10 mL volumetric flask, dilute to mark with methylene chloride. This daughter solution contains 0.1 ug/uL of B[a]P or other PAHs.

14.3.1.9 Prepare a set of standard solutions by appropriately diluting, with methylene chloride, accurately measured volumes of the daughter solution (0.1 ug/uL).

14.3.1.10 Accurately pipette 100 uL, 300 uL, 500 uL, 700 uL and 1000 uL of the daughter solution (0.1 ug/uL) into each 10 mL volumetric flask, respectively. To each of these flasks, add an internal deuterated standard to give a final concentration of 40 ng/uL of the internal deuterated standard (Section 14.3.2.1). Dilute to mark with methylene chloride.

14.3.1.11 The concentration of B[a]P in each flask is 1 ng/uL, 3 ng/uL, 5 ng/uL, 7 ng/uL, and 10 ug/uL respectively. All standards should be stored at 4°C and protected from fluorescent light and should be freshly prepared once a week or sooner if check standards indicates a problem.

14.3.1.12 Analyze a constant volume (1-3 uL) of each calibration standard and tabulate the area responses of the primary characteristic ion of each standard against the mass injected. The results may be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response

to amount injected (calibration factor) is a constant over the working range (<20% relative standard deviation, RSD), linearity through the origin may be assumed and the average ratio or calibration factor may be used in place of a calibration curve.

14.3.1.13 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 20%, the rest must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

14.3.2 Internal standard calibration procedure.

14.3.2.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. For analysis of B[a]P, the analyst should use perylene -d_{12}. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The following internal standards are suggested at a concentration of 40 ng/uL for specific PAHs:

Perylene - d_{12}	Acenaphthene - d_{10}
Benzo(a)pyrene	Acenaphthene
Benzo(k)fluoranthene	Acenaphthylene
Benzo(g,h,i)perylene	Fluorene
Dibenzo(a,h)anthracene	
Indeno(1,2,3-cd)pyrene	Naphthalene - d_8
Chrysene - d_{12}	Naphthalene
Benzo(a)anthracene	Phenanthrene -d_{10}
Chrysene	
Pyrene	Anthracene
	Fluoranthene
	Phenanthrene

14.3.2.2 A mixture of the above deuterated compounds in the appropriate concentration range are commercially available (see Section 9.3.1.5).

14.3.2.3 Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next two most intense ions as the secondary ions. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards, and a mass spectrometer tuning standard may be included in the internal standard solution used.

14.3.2.4 Prepare calibration standards at a minimum of three concentration level for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more of the internal deuterated standards to yield a resulting concentration of 40 ng/uL of internal standard and dilute to volume with methylene chloride. One of the calibration standards should be at a concentration near, but above, the minimum detection limit (MDL) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

14.3.2.5 Analyze constant amount (1-3 uL) of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound and internal standard, and calculate the response factor (RF) for each analyte using the following equation:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

Where:

A_s = Area of the characteristic ion for the analyte to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

C_{is} = Concentration of the internal standard, (ng/uL).

C_s = Concentration of the analyte to be measured, (ng/uL).

If the RF value over the working range is a constant (<20% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF. Table 5.0 outlines key ions for selected internal deuterated standards.

14.3.2.6 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

14.3.2.7 The relative retention times for each compound in each calibration run should agree within 0.06 relative retention time units.

14.4 Sample Analysis

14.4.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of capillary column as in the GC/MS procedure. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

14.4.2 Analyze the 1 mL extract (see Section 13.2) by GC/MS. The recommended GC/MS operating conditions to be used are specified in Section 14.2.

14.4.3 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/uL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

14.4.4 Perform all qualitative and quantitative measurements as described in Section 14.3. The typical characteristic ions for selective PAHs are outlined in Table 6.0. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon®-lined, for future analysis.

14.4.5 For sample analysis, the comparison between the sample and references spectrum must illustrate:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contaminatiuon or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

14.4.6 Determine the concentration of each analyte in the sample according to Sections 17.1 and 17.2.2.

14.5 GC/MS Performance Tests

14.5.1 Daily DFTPP Tuning - At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved when challenged with a 1 uL injection volume containing 50 ng of decafluorotriphenylphosphine (DFTPP). The DFTPP key ions and ion abundance criteria that must be met are illustrated in Table 3.0. Analysis should not begin until all those criteria are met. Background subtraction should be staightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Obtain a background correction mass spectra of DFTPP and check that all key ions criteria are met. If the criteria are not achieved, the analyst must retune the mass spectromete and repeat the test until all criteria are achieved. The

performance criteria must be achieved before any samples, blanks on standards are analyzed. If any key ion abundance observed for the daily DFTPP mass tuning check differs by more than 10% absolute abundance from that observed during the previous daily tuning, the instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

14.5.2 Daily 1-point Initial Calibration Check - At the beginning of each work day, a daily 1-point calibration check is performed by re-evaluating the midscale calibration standard. This is the same check that is applied during the initial calibration, but one instead of five working standards are evaluated. Analyze the one working standards under the same conditions the initial calibration curve was evaluated. Analyze 1 uL of each of the mid-scale calibration standard and tabulate the area response of the primary characteristic ion against mass injected. Calculate the percent difference using the following equation:

$$\% \text{ Difference} = \frac{RF_c - \overline{RF_I}}{\overline{RF_I}} \times 100$$

Where:

$\overline{RF_I}$ = average response factor from initial calibration using mid-scale standard.

RF_c = response factor from current verification check using mid-scale standard.

If the percent difference for the mid-scale level is greater than 10%, the laboratory should consider this a warning limit. If the percent difference for the mid-scale standard is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (<20% difference), then corrective action MUST be taken. [Note: Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.] This check must be met

before analysis begins. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before sample analysis begins.

14.5.3 12-hour Calibration Verification - A calibration standard at mid-level concentration containing B[a]P or other PAHs must be performed every twelve continuous hours of analysis. Compare the standard every 12-hours with the average response factor from the initial calibration. If the % difference for the response factor (see Section 14.5.2) is less than 20%, then the GC/MS system is operative within initial calibration values. If the criteria is not met (>20% difference), then the source of the problem must be determined and a new five-point curve MUST be generated.

14.5.4 Surrogate Recovery - Additional validation of the GC system performance is determined by the surrogate standard recovery. If the recovery of the surrogate standard deviates from 100% by not more than 20%, then the sample extraction, concentration, clean-up and analysis is certified. If it exceeds this value, then determine the cause of the problem and correct.

15. High Performance Liquid Chromatography (HPLC) Detection

15.1 Introduction

15.1.1 Detection of B[a]P by HPLC has also been a viable tool in recent years. The procedure outlined below has been written specifically for analysis of B[a]P by HPLC. However, by optimizing chromatographic conditions [(multiple detector fluorescence - excitation at 240 nm, emission at 425 nm; ultraviolet at 254 nm)] and varying the mobile phase composition through a gradient program, the following PAHs may also be quantitatified:

COMPOUND	DETECTOR[1]	COMPOUND	DETECTOR[1]
Acenaphthene	UV	Benzo(k)fluoranthene	FL
Acenaphthylene	UV	Dibenzo(a,h)anthracene	FL
Anthracene	UV	Fluoranthene	FL
Benzo(a)anthracene	FL	Fluorene	UV
Benzo(a)pyrene	FL	Indeno(1,2,3-cd)pyrene	FL
Benzo(b)fluoranthene	FL	Naphthalene	UV
Benzo[e]pyrene	FL	Phenanthrene	UV
Benzo(ghi)perylene	FL	Pyrene	FL

[1]UV= Ultraviolet
FL= Fluorescences

15.1.2 This method provides quantitative identification of the selected PAH's compounds listed above by high performance liquid chromatography. It is based on separating of compounds of a liquid mixture through a liquid chromatographic column and measuring the separated components with suitable detectors.

15.1.3 The method involves solvent exchange, with subsequent HPLC detection involving ultraviolet (UV) and fluoresence (FL) detection.

15.2 Solvent Exchange To Acetonitrile

15.2.1 To the extract in the concentrator tube, add 4 mL of acetonitrile and a new boiling chip; attach a micro-snyder column to the apparatus.

15.2.2 Increase temperature of the hot water bath to 95 to 100°C.

15.2.3 Concentrate the solvent as in Section 12.3.

15.2.4 After cooling, remove the micro-Snyder column and rinse its lower sections into the concentration tube with approximately 0.2 mL acetonitrile.

15.2.5 Adjust its volume to 1.0 mL.

15.3 HPLC Assembly

15.3.1 The HPLC system is assembled, as illustrated in Figure 10.

15.3.2 The HPLC system is operated according to the following parameters:

HPLC Operating Parameters

Guard Column:	VYDAC 201 GCCIOYT	
Analytical Column:	VYDAC 201 TP5415 C-18 RP (0.46 x 25 cm)	
Column Temperature:	27.0 ± 2°C	
Mobile Phase:	Solvent Composition	Time (Minutes)
	40% Acetonitrile/60% water	0
	100% Acetonitrile	25
	100% Acetonitrile	35
	40% Acetonitrile/60% water	45
	Linear gradient elution at 1.0 mL/min	
Detector:	Variable wavelength ultraviolet and fluorescence.	
Flow Rate:	1.0 mL/minute	

[Note: To prevent irreversible absorption due to "dirty" injections and premature loss of column efficiency, a guard column is installed between the injector and the analytical column. The guard column is generally packed with identical material as is found in the analytical column. The guard column is generally replaced with a fresh guard column after several injections (50) or when separation between compounds becomes difficult. The analytical column specified in this procedure has been laboratory evaluated. Other analytical columns may be used as long as they meet procedure and separation requirements. Table 7.0 outlines other columns uses to determine PAHs by HPLC.]

15.3.3 The mobile phases are placed in separate HPLC solvent reservoirs and the pumps are set to yield a total of 1.0 mL/minute and allowed to pump for 20-30 minutes before the first analysis. The detectors are switched on at least 30 minutes before the first analysis. UV detection at 254 nm is generally preferred. The fluorescence spectrometer excitation wavelengths range from 250 to 800 nanometers. The excitation and emission slits are both set at 10 nanometers nominal bandpass.

15.3.4 Before each analysis, the detector baseline is checked to ensure stable operation.

15.4 HPLC Calibration

15.4.1 Prepare stock standard solutions at PAH concentrations of 1.00 ug/uL by dissolving 0.0100 grams of assayed material in acetonitrile and diluting to volume in a 10 mL volumetric flask. [Note: Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 98% or greater, the weight can be used without correction to calculate the concentration of the stock standard.] Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

15.4.2 Transfer the stock standard solutions into Teflon®-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

15.4.3 Stock standard solutions must be replaced after one year, or sooner, if comparision with check standards indicates a problem.

15.4.4 Prepare calibration standards at a minimum of five concentration levels ranging from 1 ng/uL to 10 ng/uL by first diluting the stock standard 10:1 with acetonitrile, giving a daughter solution of 0.1 ug/uL. Accurately pipette 100 uL, 300 uL, 500 uL, 700 uL and 1000 uL of the daughter solution (0.1 ug/uL) into each 10 mL volumetric flask, respectively. Dilute to mark with acetonitrile. One of the concentration levels should be at a concentration near, but above, the method detection limit (MDL). The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the HPLC. [Note: Calibration standards must be replaced after six months, or sooner, if comparison with check standards indicates a problem.]

15.4.5 Analyze each calibration standard (at lease five levels) three times. Tabulate area response vs. mass injected. All calibration runs are performed as described for sample analysis in Section 15.5.1. Typical retetion times for specific PAHs are illustrated in Table 8.0. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained. The retention times for each analyte should agree within $\pm$ 2%.

15.4.6 Once linear response has been documented, an intermediate concentration standard near the anticipated levels for each component, but at least 10 times the detection limit, should be chosen for a daily calibration check. The response for the various components should be within 15% day to day. If greater variability is observed, recalibration may be required or a new calibration curve must be developed from fresh standards.

15.4.7 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_C = \frac{C_C \times V_I}{R_C}$$

Where

RF_C = response factor (usually area counts) for the component of interest in nanograms injected/ response unit.

C_C = concentration (mg/L) of analyte in the daily calibration standard.

V_I = volume (uL) of calibration standard injected.

R_C = response (area counts) for analyte in the calibration standard.

15.5 Sample Analysis

15.5.1 A 100 uL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop (10 uL) is loaded and an injection is made. The data system, if avaible, is activated simultaneously with the injection and the point of injection is marked on the strip-chart recorded.

15.5.2 After approximately one minute, the injection valve is returned to the "load" position and the syringe and valve are flushed with water in preparation for the next sample analysis.

15.5.3 After elution of the last component of interest, concentrations are calculated as described in Section 16.2.3. [Note: Table 8.0 illustrates typical retention times associates with individual PAHs, while Figure 17 represent a typical chromatogram associates with fluorescence detection.]

15.5.4 After the last compound of interest has eluted, establish a stable baseline; the system can be now used for further sample analyses as described above.

15.5.5 If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

15.5.6 Calculate surrogate standard recovery on all samples, blanks and spikes. Calculate the percent difference by the following equation:

$$\% \text{ difference} = \frac{S_R - S_I}{S_I} \times 100$$

Where

S_I = surrogate injected, ng.
S_R = surrogate recovered, ng.

15.5.7 Once a minimum of thirty samples of the same matrix have been analyzed, calculte the averge percent recovery (%R) and standard deviation of the percent recovery (SD) for the surrogate.

15.5.8 For a given matrix, calculate the upper and lower control limit for method performance for the surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = (%R) + 3(SD)

Lower Control Limit (LCL) = (%R) - 3(SD)

The surrogate recovery must fall within the control limits. If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

15.5.9 Determine the concentration of each analyte in the sample according to Sections 17.1 and 17.2.3.

15.6 HPLC System Performance

15.6.1 The general appearance of the HPLC system should be similar to that illustrated in Figure 10.

15.6.2 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \quad \frac{t^2}{W_{1/2}}$$

where:

N = column efficiency (theoretical plates).

t_r = retention time (seconds) of analyte.

$W_{1/2}$ = width of component peak at half height (seconds).

A column efficiency of >5,000 theoretical plates should be obtained.

15.6.3 Precision of response for replicate HPLC injections should be ±10% or less, day to day, for analyte calibration standards at 1 ug/mL or greater levels. At 0.5 ug/mL level and below, precision of replicate analyses could vary up to 25%. Precision of retention times should be ±2% on a given day.

15.6.4 From the calibration standards, area responses for each PAH compound can be used against the concentrations to establish working calibration curves. The calibration curve must be linear and have a correlation coefficient greater than 0.98 to be acceptable.

15.6.5 The working calibration curve should be checked daily with an analysis of one or more calibration standards. If the observed response (r_p) for any PAH varies by more than 15% from the predicted response (r_p), the test method must be repeated with new calibration standards. Alternately a new calibration curve must be prepared. [Note: If $\frac{r_o - r_p}{r_p}$ >15%, recalibration is necessary.]

15.7 HPLC Method Modification

15.7.1 The HPLC procedure has been automated by Acurex Corporation as part of their "Standard Operating Procedure for Polynuclear Aromatic Hydrocarbon Analysis by High Performance Liquid Chromatography Methods," as reported in Reference 9 of Section 18.

15.7.2 The system consists of a Spectra Physics 8100 Liquid Chromatograph, a micro-processor-controlled HPLC, a ternary gradient generator, and an autosampler (10 uL injection loop).

15.7.3 The chromatographic analysis involves an automated solvent program allowing unattended instrument operation. The

solvent program consists of four timed segments using varying concentrations of acetonitrile in water with a constant flow rate, a constant column temperature, and a 10-minute equilibration time, as outlined below.

AUTOMATED HPLC WORKING PARAMETERS

Time	Solvent Composition	Temperature	Rate
10 minutes equilibration	40% Acetonitrile 60% Water	27.0 ± 2°C	1 mL/min
T=0	40% Acetonitrile 60% Water		
T=25	100% Acetonitrile		
T=35	100% Acetonitrile		
T=45	40% Acetonitrile 60% Water		

Table 9.0 outlines the associated PAHs with their minimum detection limits (MDL) which can be detected employing the automated HPLC methodology.

15.7.4 A Vydac or equivalent analytical column packed with a C_{18} bonded phase is used for PAH separation with a reverse phase guard column. The optical detection system consists of a Spectra Physics 8440 variable Ultraviolet (UV)/Visible (VIS) wavelength detector and a Perkin Elmer LS-4 Fluorescence Spectrometer. The UV/VIS detector, controlled by remote programmed commands, contains a Deuterium lamp with wavelength selection between 150 and 600 nanometers. It is set at 254 nanometers with the time constant (detector response) at 1.0 seconds.

15.7.5 The LS-4 Fluorescence Spectrometer contains separate excitation and emission monochromators which are positioned by separate microprocessor-controlled stepper motors. It contains a Xenon discharge lamp, side-on photomultiplier and a 3-microliter illuminated volume flow cell. It is equipped with a wavelength programming facility to set the monochromators automatically to a given wavelength position. This greatly enhances selectivity by changing

the fluorescence excitation and emission detection wavelengths during the chromatographic separation in order to optimize the detection of each PAH. The excitation wavelengths range from 230 to 720 nanometers; the emission wavelengths range from 250 to 800 nanometes. The excitation and emission slits are both set at 10 nanometers nominal bandpass.

15.7.6 The UV detector is used for determining naphthalene, acenaphthylene and acenapthene, and the fluorescence detector is used for the remaining PAHs. Table 9 outlines the detection techniques and minimum detection limit (MDL) employing this HPLC system. A Dual Channel Spectra Physics (SP) 4200 computing integrator, with a Labnet power supply, provides data analysis and a chromatogram. An IBM PC XT with a 10-megabyte hard disk provides data storage and reporting. Both the SP4200 and the IBM PC XT can control all functions of the instruments in the series through the Labnet system except for the LS-4, whose wavelength program is started with a signal from the High Performance Liquid Chromatograph autosampler when it injects. All data are transmitted to the XT and stored on the hard disk. Data files can later be transmitted to floppy disk storage.

16. Quality Assurance/Quality Control

16.1 General System QA/QC

16.1.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate a typical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

16.1.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent solvent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent solvent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

16.1.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike and deuterated/surrogate samples must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

16.1.4 The experience of the analyst performing gas chromatography and high performance liquid chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response windows obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., column changed), recalibration of the system must take place.

16.2 Process, Field, and Solvent Blanks

16.2.1 One cartridge (XAD-2 or PUF) and filter from each batch of approximately twenty should be analyzed, without shipment to the field, for the compounds of interest per to serve as a process blank. A blank level of less than 10 ng per cartridge/filter assembly for single PAH component is considered to be acceptable.

16.2.2 During each sampling episode, at least one cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

16.2.3 During the analysis of each batch of samples at least one solvent process blank (all steps conducted but no cartridge or filter included) should be carried through the procedure and analyzed. Blank levels should be less than 10 ng/sample for single components to be acceptable.

16.2.4 Because the sampling configuration (filter and backup adsorbent) has been tested for targeted PAHs in the laboratory in relationship to collection efficiency and has been demonstrated to be greater than 95% for targeted PAHs, no field recovery evaluation will occur as part of the QA/QC program outlined in this section.

16.3 Gas Chromatography with Flame Ionization Detection

16.3.1 Under the calibration procedures (internal and external), the % RSD of the calibration factor should be <20% over the linear working range of a five point calibration curve (Sections 13.4.1.6 and 13.4.2.6).

16.3.2 Under the calibration procedures (internal and external), the daily working calibration curve for each analyte should not vary from the predicted response by more than $\pm$20% (Sections 13.4.1.7 and 13.4.2.8).

16.3.3 For each analyte, the retention time window must be established (Section 13.5.1), verified on a daily basis (Section 13.6.3.2) and established for each analyte throughout the course of a 72-hour period (Section 13.5.3).

16.3.4 For each analyte, the mid-level standard must fall within the retention time window on a daily basis as a qualitative performance evaluation of the GC system (Section 13.6.3.4).

16.3.5 The surrogate standard recovery must not deviate from 100% by no more than 20% (Section 13.6.3.5).

16.4 Gas Chromatography with Mass Spectroscopy Detection

16.4.1 Section 14.5.1 requires the mass spectrometer be tuned daily with DFTPP and meet relative ion abundance requirements outlined in Table 3.

16.4.2 Section 14.3.1.1 requires a minimum of five concentration levels of each analyte (plus deuterated internal standards) be prepared to establish a calibration factor to illustrate <20% variance over the linear working range of the calibration curve.

16.4.3 Section 14.3.1.13 requires the verification of the working curve each working day (if using the external standard technique) by the measurement of one or more calibration standards. The predicted response must not vary by more than ±20%.

16.4.4 Section 14.3.2.6 requires the initial calibration curve be verified each working day (if using the internal standard technique) by the measurement of one or more calibration standards. If the response varies by more than ±20% of predicted response, a fresh calibration curve (five point) must be established.

16.4.5 Section 14.4.5 requires that for sample analysis, the comparison between the sample and reference spectrum illustrate:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in sample the spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contaminatiuon or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

16.4.6 Section 14.5.3 requires that initial calibration curve be verified every twelve continuous hour of analysis by a mid-level calibration standard. The response must be less than 20% difference from the initial response.

16.4.7 The surrogate standard recovery must not deviate from 100% by no more than 20% (Section 14.5.4).

16.5 High Performance Liquid Chromatography

16.5.1 Section 15.4.4 requires the preparation of calibration standards at a minimum of five concentration levels to establish correlation coefficient of at least 0.999 for a linear least-squares fit of the data.

16.5.2 Section 15.4.5 requires that the retention time for each analyte should agree within ±2%.

16.5.3 A daily calibration check involving an intermediate standard of the initial five point calibration curve should be within ±15% from day to day.

16.5.4 Section 15.5.6 requires the calculation of percent difference of surrogate standard recovery in order to establish control limits:

Upper Control Limit (UCL) = (%R) + 3 (SD)
Lower Control Limit (LCL) = (%R) - 3 (SD)

The surrogate recovery must fall within the control limits.

17. Calculations

17.1 Sample Volume

17.1.1 The total sample volume should be corrected to standard temperature and pressure.

17.1.2 The total sample volume (V_m) is calculated from the periodic flow readings (Magnehelic readings taken in Section 11.3.13) using the following equation.

$$V_m = \frac{Q_1 + Q_2 \ldots Q_n}{N} \times \frac{T}{1000}$$

Where

V_m = total sample volume (m^3) at ambient conditions.

$Q_1, Q_2 \ldots Q_n$ = flow rates determined at the beginning, end, and intermediate points during sampling (m3/minute).

N = number of data points.

T = elapsed sampling time (minutes).

17.1.3 The volume of air sampled can be converted to standard conditions (760 mm Hg pressure and 25°C) using the following equation:

$$V_S = V_m \times \frac{p_A}{760} \times \frac{298}{273 + t_A}$$

Where

V_S = total sample volume (m^3) at standard temperature and pressure (25°C and 760 mm Hg pressure).

V_m = total sample flow under ambient conditions (m^3).

p_A = ambient pressure (mm Hg).

t_A = ambient temperature (°C).

17.2 Sample Concentration

17.2.1 GC/FI Detection

17.2.1.1 The concentration of each analyte in the sample may be determined from the external standard technique by calculating the amount of standard injected, from the peak response, using the calibration curve or the calibration factor determined in Section 13.4.1.6.

17.2.1.2 The concentration of a specific analyte is calculated as follows:

$$\text{Concentration, ng/m}^3 = \frac{[(A_x)(V_t)(D)]}{[(CF)(V_i)(V_s)]}$$

Where:

CF = calibration factor for chromatographic system, peak height or area response per mass injected, Section 13.4.1.6.

A_x = Response for the analyte in the sample, area counts or peak height.

V_t = volume of total sample, uL.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D=1, dimensionless

V_i = volume of sample injected, uL

V_s = total sample volume (m^3) at standard temperature and pressure (25°C and 760 mm Hg), Section 17.1.3.

17.2.2 GC/MS Detection

17.2.2.1 When an analyte has been identified, the quantification of that analyte will be based on the integrated abundance from the monitoring of the primary characteristic ion. Quantification will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (see Section 14.3.2.1).

17.2.2.2. Calculate the concentration of each identified analyte in the sample as follows:

$$\text{Concentration, ng/m}^3 = \frac{[(A_x)(I_s)(V_t)(D)]}{[(A_{is})(RF)(V_i)(V_s)]}$$

Where

A_x = area of characteristic ion(s) for analyte being measured.

I_s = amount of internal standard injected, ng.

V_t = volume of total sample, uL.

D = dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = area of characteristic ion(s) for internal standard.

RF = Response factor for analyte being measured, Section 14.3.2.5.

V_i = volume of analyte injected, uL.

V_s = total sample volume (m^3) at standard temperature and pressure (25°C and 760 mm Hg), Section 17.1.3.

17.2.3 HPLC Detection

17.2.3.1 The concentration of each analyte in the sample may be determined from the external standard technique by calculating response factor and peak response using the calibration curve.

17.2.3.2 The concentration of a specific analyte is calculated as follows:

$$\text{Concentration, ng/m}^3 = \frac{[(RF_c)(A_x)(V_t)(D)]}{[(V_i)(V_s)]}$$

Where

RF_c = response factor (nanograms injected per area counts) calculated in Section 15.4.7.

A_x = response for the analyte in the sample, area counts or peak height.

V_t = volume of total sample, uL.

D = dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

V_i = volume of sample injected, uL.

V_s = total sample volume (m^3) at standard temperature and pressure (25°C and 760 mm Hg), Section 17.1.3.

17.3 Sample Concentration Conversion From ng/m^3 to ppbv

17.3.1 The concentrations calculated in Section 17.2 can be converted to ppbv for general reference.

17.3.2 The analyte concentration can be converted to ppbv using the following equation:

$$C_A \text{ (ppbv)} = C_A \text{ (ng/m}^3\text{)} \times \frac{24.4}{MW_A}$$

Where

C_A = concentration of analyte, ng/m^3, calculated according to Sections 17.2.1 through 17.2.3.

MW_A = molecular weight of analyte, g/g-mole

24.4 = molar volume occupied by ideal gas at standard temperature and pressure (25°C and 760 mm Hg), l/mole.

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TABLE 1.0 FORMULAE AND PHYSICAL PROPERTIES OF SELECTIVE PAHs

	FORMULA	MOLECULAR WEIGHT	MELTING POINT °C	BOILING POINT °C	CASE #
Acenaphthene	$C_{12}H_{10}$	154.21	96.2°	279	83-32-9
Acenaphthylene	$C_{12}H_{8}$	152.20	92-93	265-275	208-96-8
Anthracene	$C_{14}H_{10}$	178.22	218°	342	120-12-7
Benzo(a)anthracene	$C_{18}H_{12}$	228.29	158-159	-	56-55-3
Benzo(a)pyrene	$C_{20}H_{12}$	252.32	177°	310-312	50-32-8
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.32	168	-	205-99-2
Benzo(e)pyrene	$C_{20}H_{12}$	252.32	178-179	-	192-92-2
Benzo(g,h,i)perlene	$C_{22}H_{12}$	276.34	273	-	191-24-2
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.32	217	480	207-08-9
Chrysene	$C_{18}H_{12}$	228.29	255-256	-	218-01-9
Dibenzo(a,h)anthracene	$C_{22}H_{14}$	278.35	262	-	53-70-3
Fluoranthene	$C_{16}H_{10}$	202.26	110	-	206-44-0
Fluorene	$C_{13}H_{10}$	166.22	116-117	293-295	86-73-7
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.34	161.5-163	-	193-39-5
Naphthalene	$C_{10}H_{8}$	128.16	80.2	217.9	91-20-3
Phenanthrene	$C_{14}H_{10}$	178.22	100°	340	85-01-8
Pyrene	$C_{16}H_{10}$	202.26	156	399	129-00-0

*Many of these compounds sublime.

TABLE 2.0 RETENTION TIMES FOR SELECTIVE PAHs FOR PACKED AND CAPILLARY COLUMNS

Compound	Packed[1]	Capillary[2]
Acenaphthene	10.8	16.8
Acenaphthylene	10.4	15.9
Anthracene	15.9	20.7
Benzo(a)anthracene	20.6	29.1
Benzo(a)pyrene	29.4	36.2
Benzo(b)fluoranthene	28.0	34.2
Benzo(ghi)perylene	38.6	48.4
Benzo(k)fluoranthene	28.0	34.4
Chrysene	24.7	29.3
Dibenzo(a,h)anthracene	36.2	46.1
Fluoranthene	19.8	24.3
Fluorene	12.6	18.1
Indeno(1,2,3-cd)pyrene	36.2	45.6
Naphthalene	4.5	11.0
Phenanthrene	15.9	20.6
Pyrene	20.6	25.0

[1]GC conditions: Chromosorb W-AW-DMCS (100/120 mesh) coated with 3% OV-17, packed in a 1.8-m long x 2 mm ID glass column, with nitrogen carrier gas at a flow rate of 40 mL/min. Column temperature was held at 100°C for 4 min. then programmed at 8°/minute to a final hold at 280°C.

[2]Capillary GC conditions: 30 meter fused silica SPB-5 capillary column; flame ionization detector, splitless injection; oven temperature held at 80 degrees C for 2 minutes, increased at 8 degrees/min. to 280 degrees C.

TABLE 3.0 DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

TABLE 4.0 GC AND MS OPERATING CONDITIONS

Chromatography	
Column	Hewlett-Packard Ultra #2 crosslinked 5% phenyl methyl silicone (50 m x 0.25 mm, 0.25 um film thickness) or equivalent
Carrier Gas	Helium velocity 20 cm^3/sec at 250°C
Injection Volume	Constant (1-3 uL)
Injection Mode	Splitless
Temperature Program	
Initial Column Temperature	45°C
Initial Hold Time	1 min
Program	45°C to 100°C in 5 min, then 100°C to 320°C at 8°C/min
Final Hold Time	15 min
Mass Spectrometer	
Detection Mode	Multiple ion detection, SIM mode

TABLE 5.0 CHARACTERISTIC IONS FROM GC/MS DETECTION FOR DEUTERATED INTERNAL STANDARDS AND SELECTED PAHs

Compound	M/Z
D_8-naphthalene	136
D_{10}-phenanthrene	188
Phenathrene	178
Anthracene	178
Fluoranthene	202
D_{10}-pyrene	212
Pyrene	202
Cyclopenta[c,d]pyrene	226
Benz[a]anthracene	228
D_{12}-chrysene	240
Benzo[e]pyrene	252
D_{12}-benzo[a]pyrene	264
Benzo[a]pyrene	252

TABLE 6.0 CHARACTERISTIC IONS FROM GC/MS DETECTION FOR SELECTED PAHs

Compound	Primary		Secondary
Acenaphthene	154	153	152
Acenaphthylene	152	151	153
Anthracene	178	179	176
Benzo(a)anthracene	228	229	226
Benzo(a)pyrene	252	253	125
Benzo(b)fluoranthene	252	253	125
Benzo(ghi)perylene	276	138	277
Benzo(k)fluoranthene	252	253	125
Chrysene	228	226	229
Dibenzo(a,h)anthracene	278	139	279
Fluoranthene	202	101	203
Fluorene	166	165	167
Indeno(1,2,3-cd)pyrene	276	138	227
Naphthalene	128	129	127
Phenanthrene	178	179	176
Pyrene	202	200	203

TABLE 7.0. COMMERCIAL AVAILABLE COLUMNS FOR PAH ANALYSIS USING HPLC

Company	Column Identification	Column Name
The Separation Group P.O. Box 867 Hesperia, California 92345	201-TP	VYDAC
Rainin Instrument Company Mack Road Wasurn, MA 01801-4626	Ultrasphere - ODS	ALEX
Supelco, Inc. Supelco Park Bellefonte, PA 16823-0048	LC-PAH	Supelcosil
DuPont Company Biotechnology Systems Barley Mill Plaza, P24 Wilmington, DE 19898	ODS	Zorbax
Perkin-Elmer Corp. Corporate Office Main Avenue Norwalk, CT 06856	HC-ODS	Sil-X
Waters Associates 34-T Maple St. Milford, MA 01757	u-Bondapak	NH_3 u-Bondapak

TABLE 8.0. TYPICAL RETENTION TIME FOR SELECTIVE PAHs BY HPLC SEPARATION AND DETECTION

Compound	Retention Times (minutes) HPLC Conditions			
	Condition A		Condition B	
	Fluorescence	UV	Fluorescence	UV
Acenaphthene		20.5		18.0
Acenaphthylene		18.5		15.8
Anthracene	23.4		21.0	21.0
Benzo(a)anthracene	28.5		26.3	26.3
Benzo(a)pyrene	33.9		31.1	31.1
Benzo(b)fluoranthene	31.6		29.3	29.3
Benzo(e)pyrene			31.1	
Benzo(ghi)perylene	36.3		33.9	33.9
Benzo(k)fluoranthene	32.9		30.2	30.2
Chrysene	29.3		26.7	
Dibenzo(a,h)anthracene	35.7		32.7	32.7
Fluoranthene	24.5		22.5	22.5
Fluorene		21.2	18.5	18.5
Indeno(1,2,3-cd)pyrene	37.4		34.6	34.6
Naphthalene		16.6		14.0
Phenanthrene	22.1		19.9	19.9
Pyrene	25.4		23.4	23.4

Condition A HPLC parameters: Reverse phase HC-ODS Sil-X, 5 micron particle size, in a 250-mm x 2.6-mm I.D. stainless steel column. Isocratic elution for 5 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

Condition B HPLC parameters: Reverse phase VYDAC 201 TP 5415, 5 micron particle size, in a .46 x 25 cm stainless steel column. Isocratic elution for 10 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile for 10 minutes then linear gradient to 40/60 acetonitrile for 10 minutes at 15 mL/min.

TABLE 9.0. RETENTION TIMES (RT) AND MINIMUM DETECTION LIMITS (MDLs) FOR SELECTED PAHs USING ULTRAVIOLET AND FLOURESCENCE DETECTION

	Ultraviolet Detector		Flourescence Detector	
PAH	RT	MDL	RT	MDL
Naphthalene	14.0	250pg/uL		
Acenaphthylene	15.85	250pg/uL		
Acenaphthene	18.0	250pg/uL		
Fluorene	18.5	50pg/uL	18.5	5pg/uL
Phenanthrene	19.9	50pg/uL	19.9	10pg/uL
Anthracene	21.0	50pg/uL	21.0	50pg/uL
Fluoranthene	22.5	50pg/uL	22.5	10pg/uL
Pyrene	23.4	50pg/uL	23.4	5pg/uL
Benzo(a)anthracene	26.3	50pg/uL	26.3	5pg/uL
Chrysene	26.7	50pg/uL	26.7	5pg/uL
Benzo(b)fluoranthene	29.3	50pg/uL	29.3	10pg/uL
Benzo(k)fluoranthene	30.2	50pg/uL	30.2	5pg/uL
Benzo(a)pyrene	31.1	50pg/uL	31.1	5pg/uL
Dibenzo(a,h)anthracene	32.7	50pg/uL	32.7	5pg/uL
Benzo(ghi)perylene	33.9	50pg/uL	33.9	5pg/uL
Indeno(1,2,3-cd)pyrene	34.6	50pg/uL	34.6	50pg/uL

RT = Retention time in minutes
MDL = Minimum detection limit

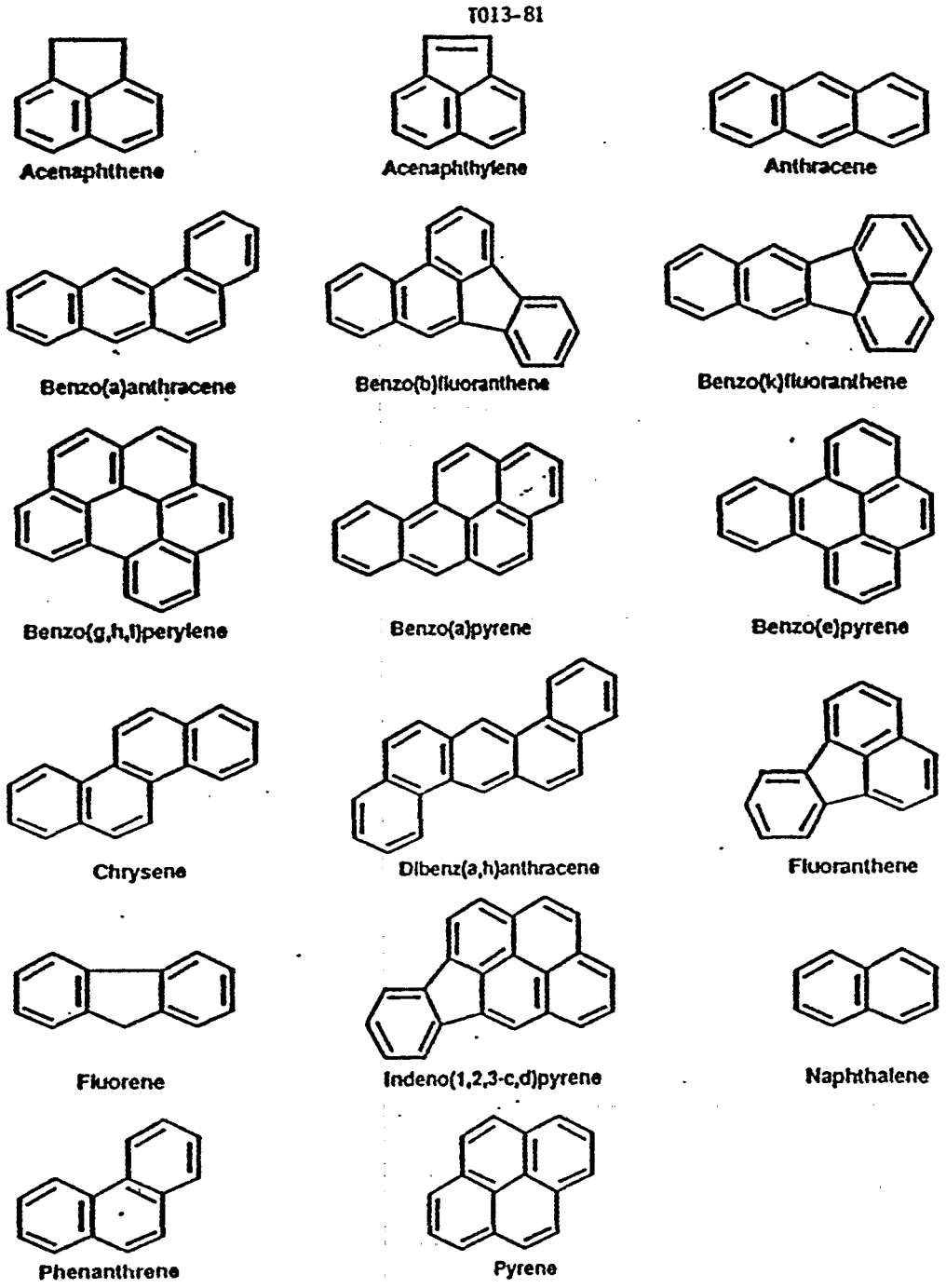


FIGURE 1.0 RING STRUCTURE OF SELECTIVE PAHs.

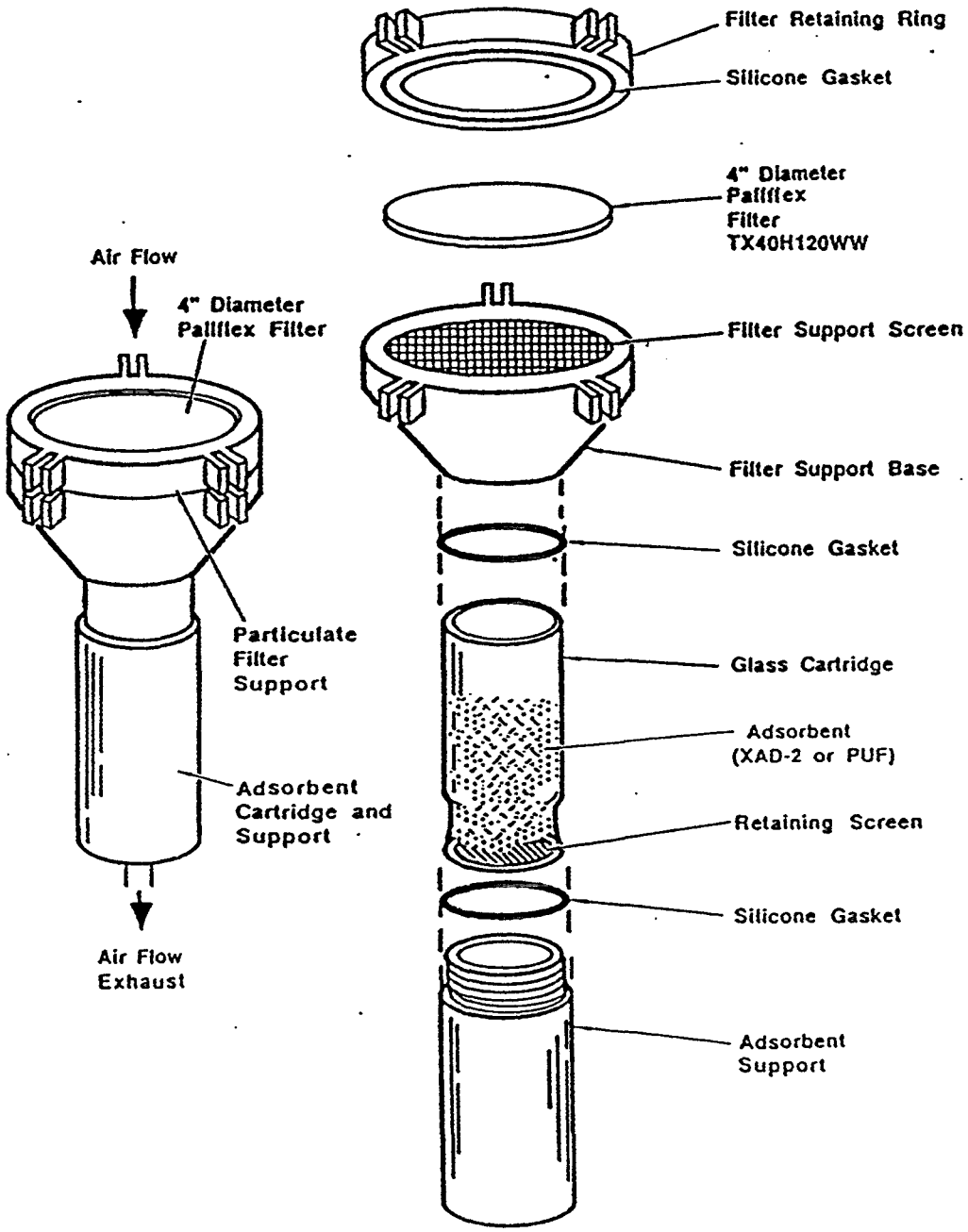


FIGURE 2.0 GENERAL METAL WORKS SAMPLING HEAD

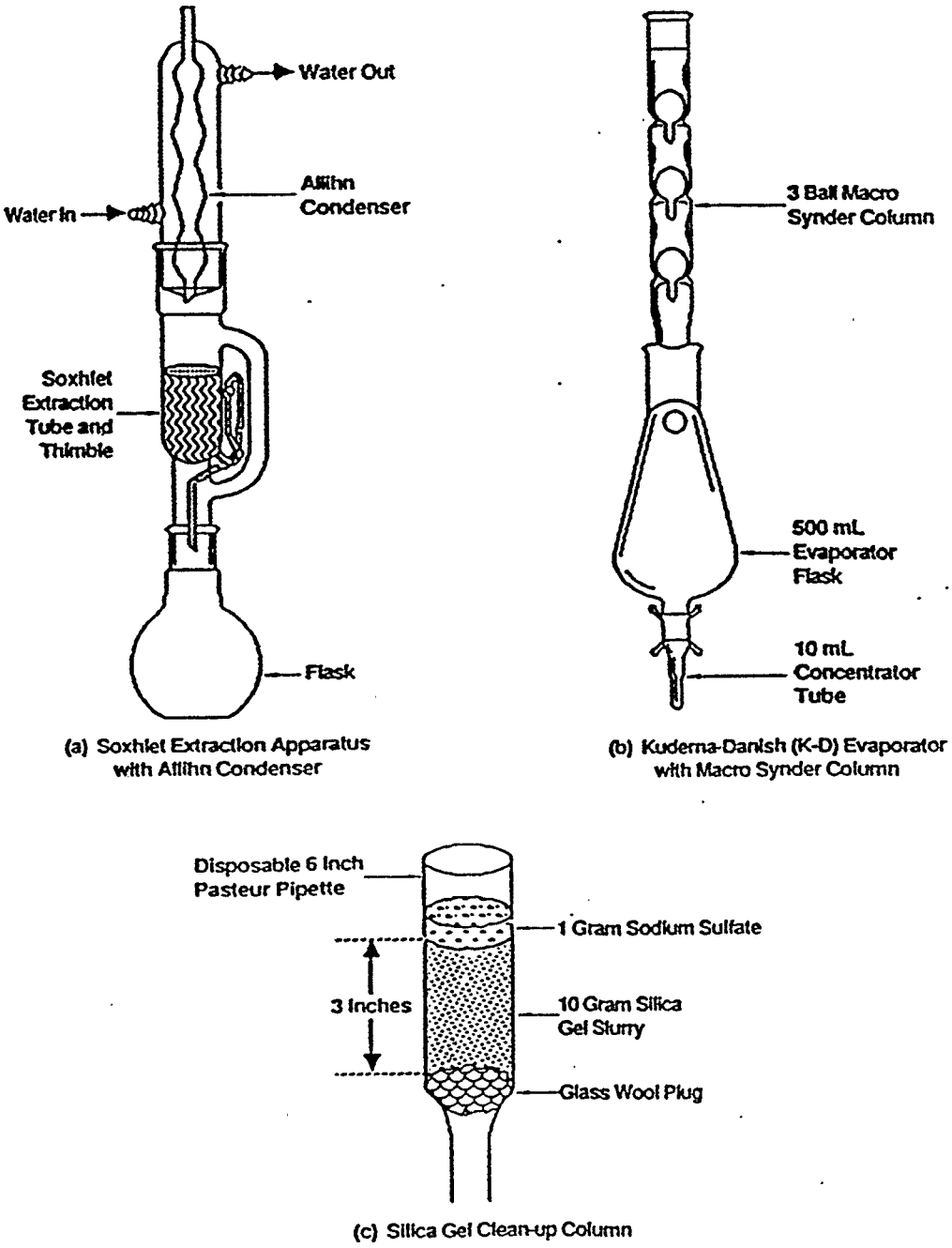


FIGURE 3. APPARATUS USES IN SAMPLING ANALYSIS.

APPENDIX D

EPA METHOD TO4

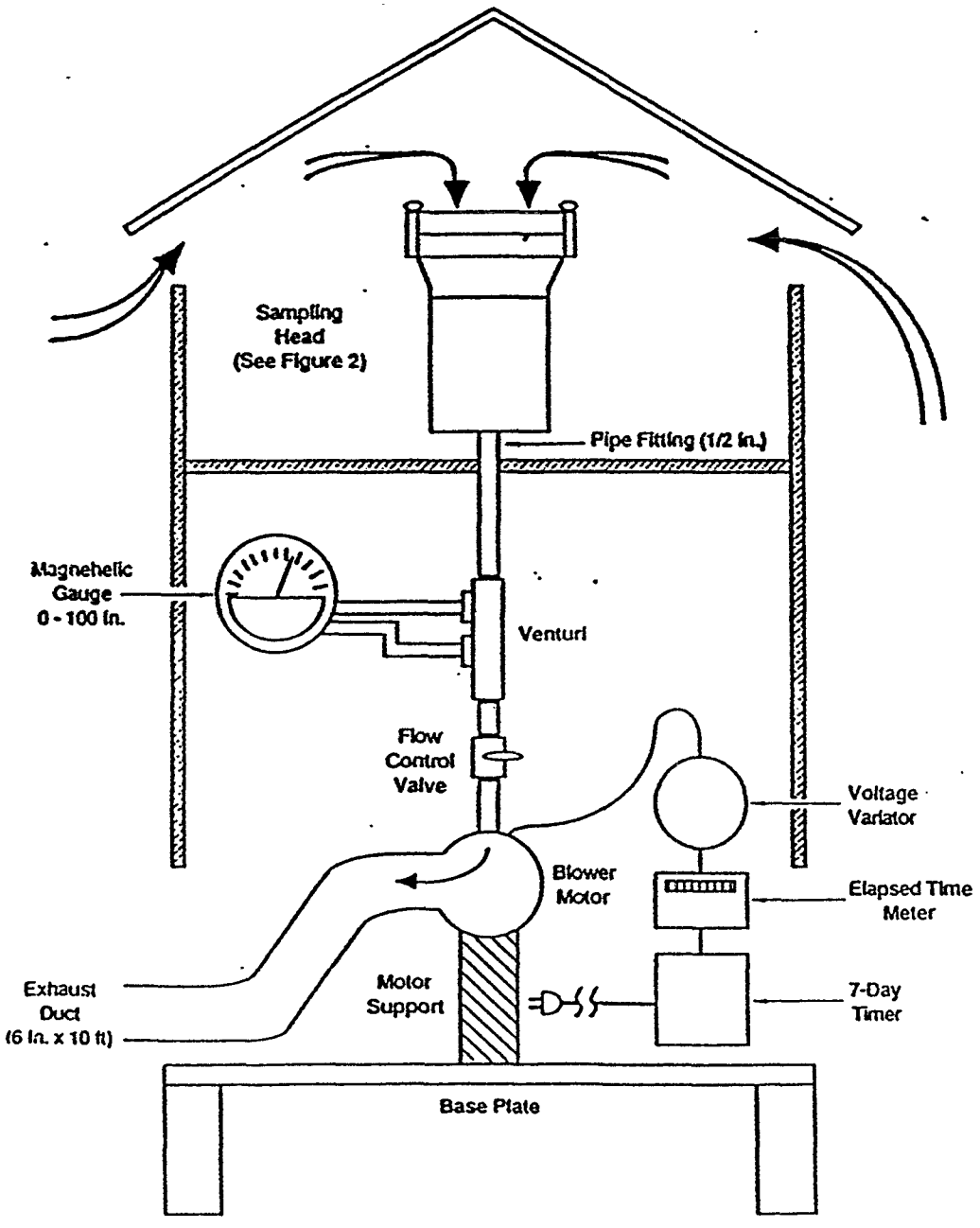


FIGURE 4. MODIFIED HIGH VOLUME AIR SAMPLER
GENERAL METAL WORKS MODEL PS-1 SAMPLER

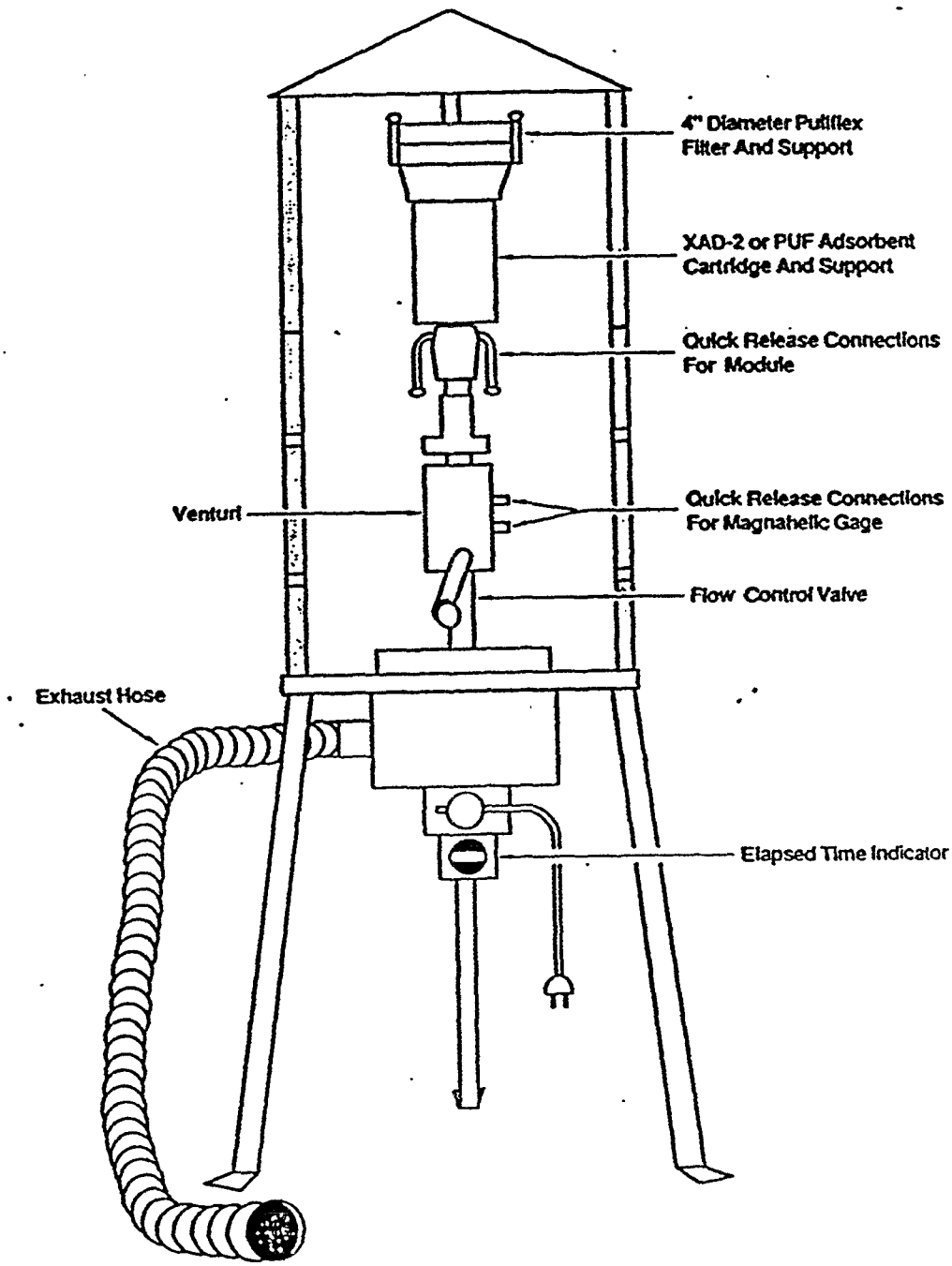


FIGURE 5. PORTABLE HIGH VOLUME AIR SAMPLER

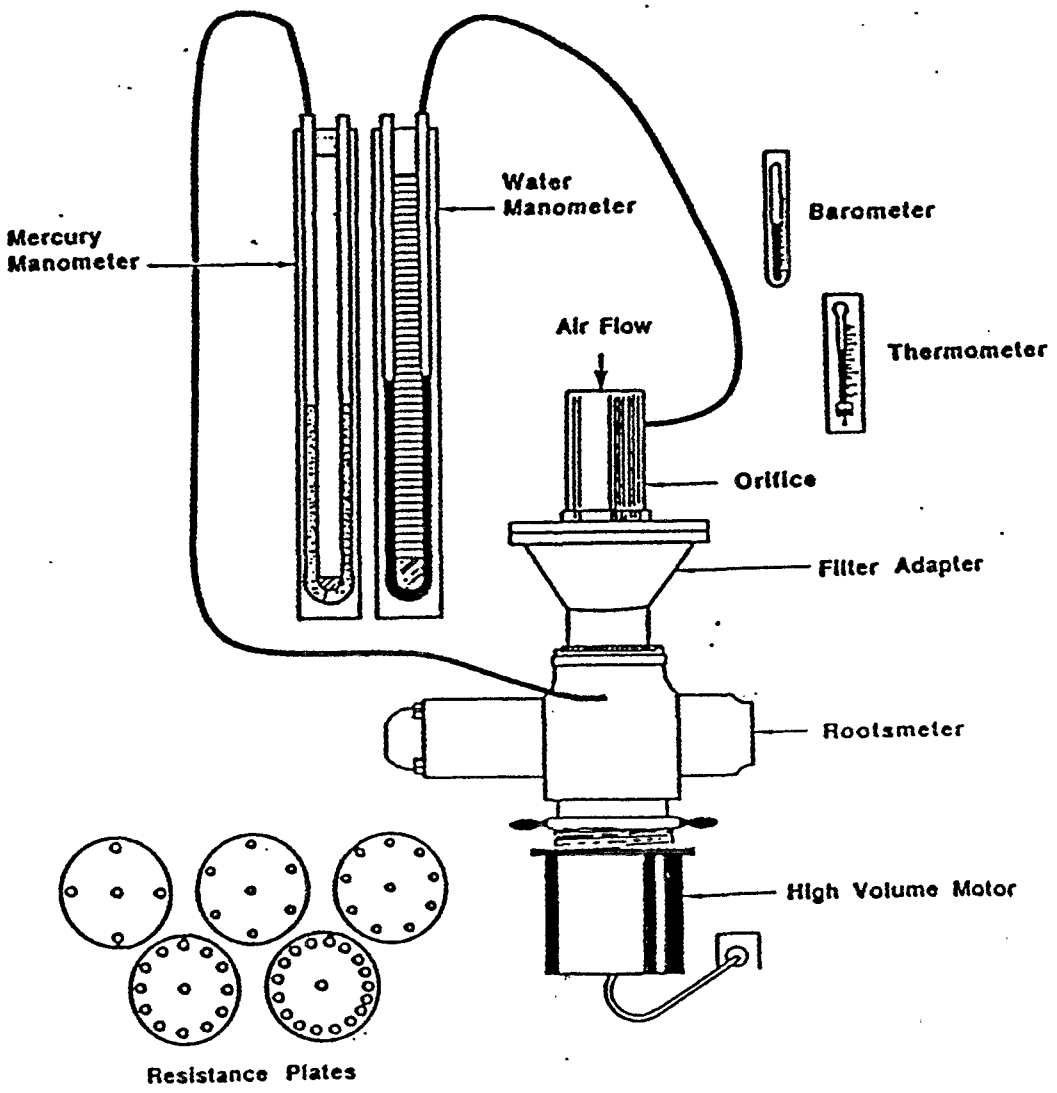


FIGURE 6. LABORATORY ORIFICE CALIBRATION SETUP

T_1 _____ °C _____ K

P_1 _____ mmHg

Orifice No. _____

Roots Meter No. _____

Name _____

Date _____

Resistance Plates (No. of Holes)	Air Volume Measured By Rootsmeter V_m		Standard Volume V_{std} (std m^3)	Time For Air Volume To Pass Through Rootsmeter Θ (min)	Roots Meter Pressure Differential ΔP (mm Hg)	Pressure Drop Across Orifice ΔH (in. H_2O)	x-Axis Standard Flow Rate Q_{std} (std m^3/min)	y-Axis $\sqrt{\Delta H(P_1 / P_{std})(298 / T_1)}$ Value
	(ft^3)	(m^3)						
5	200	5.66						
7	200	5.66						
10	300	8.50						
13	300	8.50						
18	300	8.50						

Factors: $(ft^3)\left(0.02832 \frac{m^3}{ft^3}\right) = m^3$ and (in. Hg) $25.4\left(\frac{mm\ Hg}{in.\ Hg}\right) = mm\ Hg$.

Calculation Equations: 1. $V_{std} = V_m \left(\frac{P_1 - \Delta P}{P_{std}}\right)\left(\frac{T_{std}}{T_1}\right)$ Where: $T_{std} = 298\ K$, $P_{std} = 760.0\ mm\ Hg$ 2. $Q_{std} = \frac{V_{std}}{\Theta}$

FIGURE 7. ORIFICE CALIBRATION DATA SHEET.

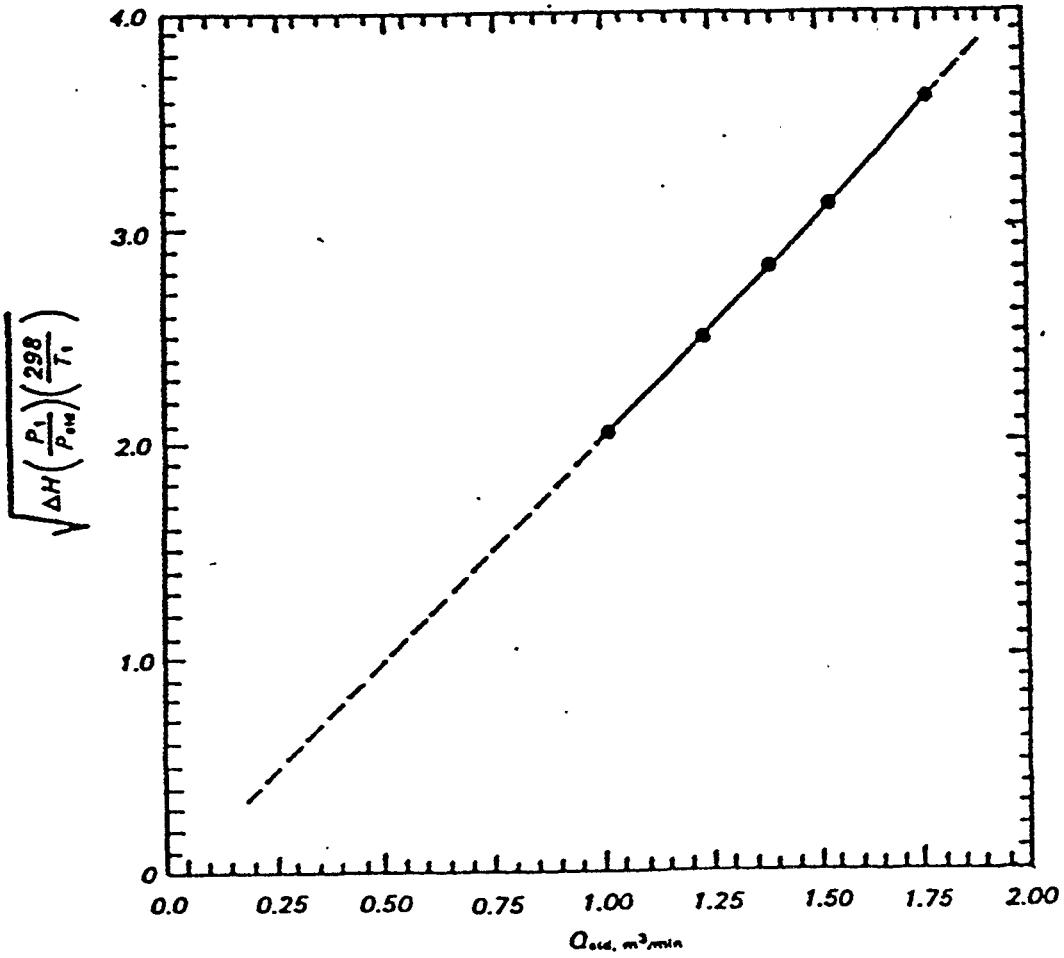


FIGURE 8. ORIFICE METER CALIBRATION CURVE

Performed by _____ Calibration Orifice _____ S/N _____ Ambient Temperature _____ ° C

Date/Time _____ Manometer S/N _____ Bar. Press. _____ mm Hg

Sampler S/N	Variac Setting V	Timer OK? Yes/No	Flow Rate Transfer Standard		Sampler Venturi Data		Comments
			Manometer in. H_2O	Q_{std} [a]	Magnehelic, in. H_2O	Q_{ms} [b]	

[a] From Calibration Curve For Flow Rate Transfer Standard (Section 11.2.1).

[b] From Calibration Curve for Venturi Tube Using Flow Rate Transfer Standard (Section 11.2.2.9).

FIGURE 9. FIELD CALIBRATION DATA SHEET

Sampler Site _____

Sampler Location _____

Date _____

	Before	After
Barometric Pressure		
Ambient Temperature		

Site _____ Date _____ Performed By _____

Sampler S/N	Sampling Location I.D.	Height Above Ground	Identification No.		Sampling Period		Totaling Sampling Time, min.	Pump Timer Hr. Min.	Sampler Flow Check[1]				
			Filter	XAD-2 or PUF	Start	Stop			Manometer Δ H, Inches of Water	Q_{xs}	M	Q_{ms}	Within ± 10%

[1] Must Be Performed Before and After Each Sampling Period

Checked By _____

Date _____

FIGURE 10. FIELD TEST DATA SHEET.

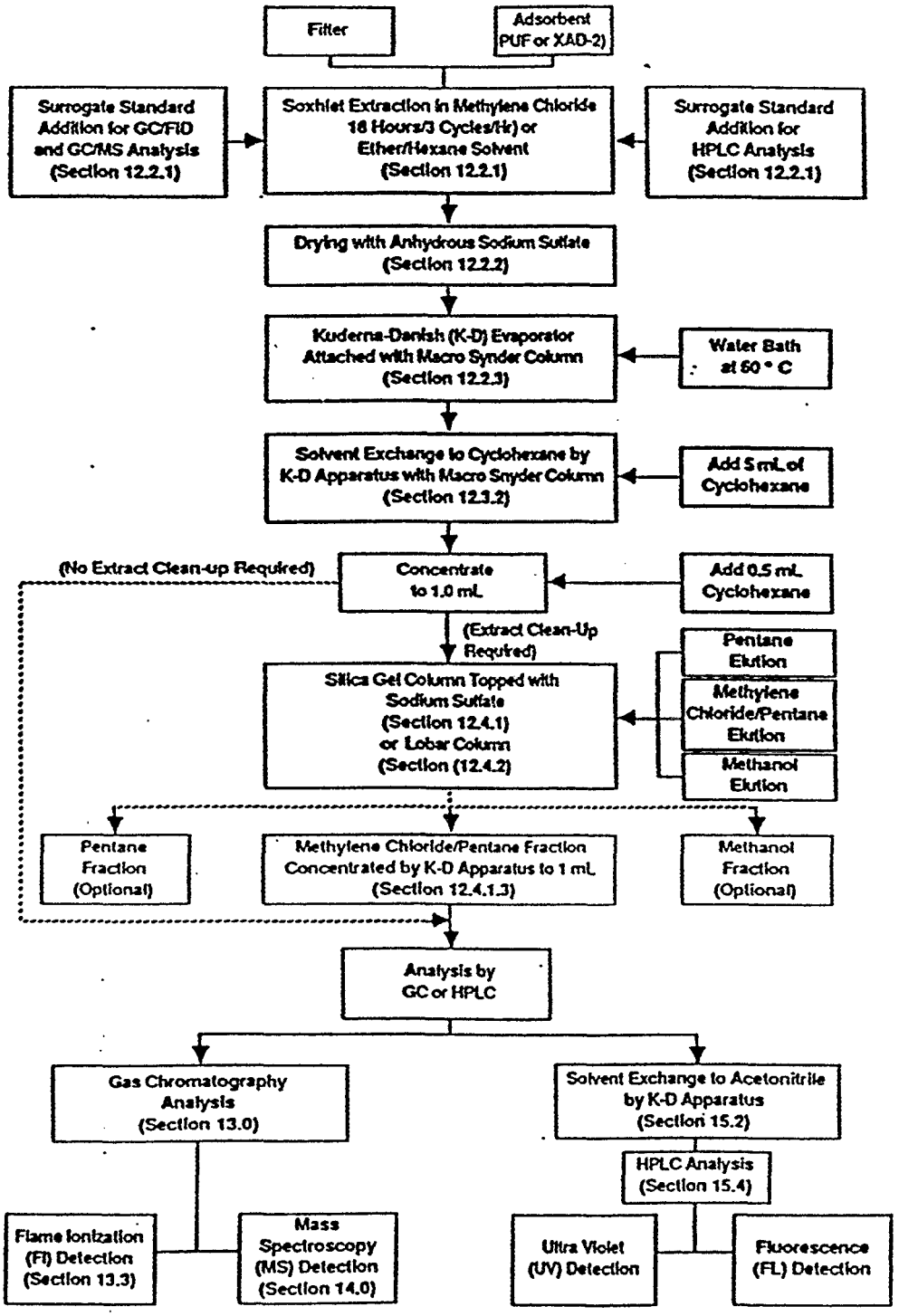


FIGURE 11.0. SAMPLE CLEAN-UP, CONCENTRATION, SEPARATION AND ANALYSIS SEQUENCE.

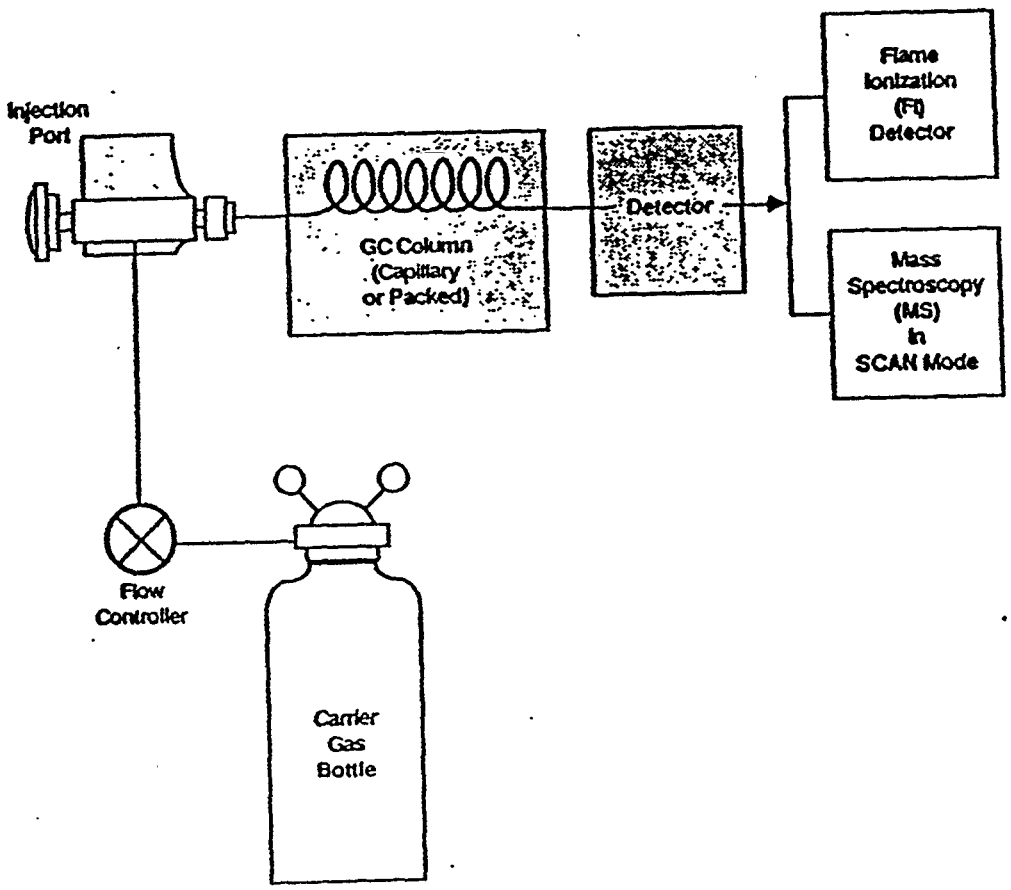


FIGURE 12.0 GC SEPARATION WITH SUBSEQUENT FLAME IONIZATION (FI) OR MASS SPECTROSCOPY (MS) DETECTION.

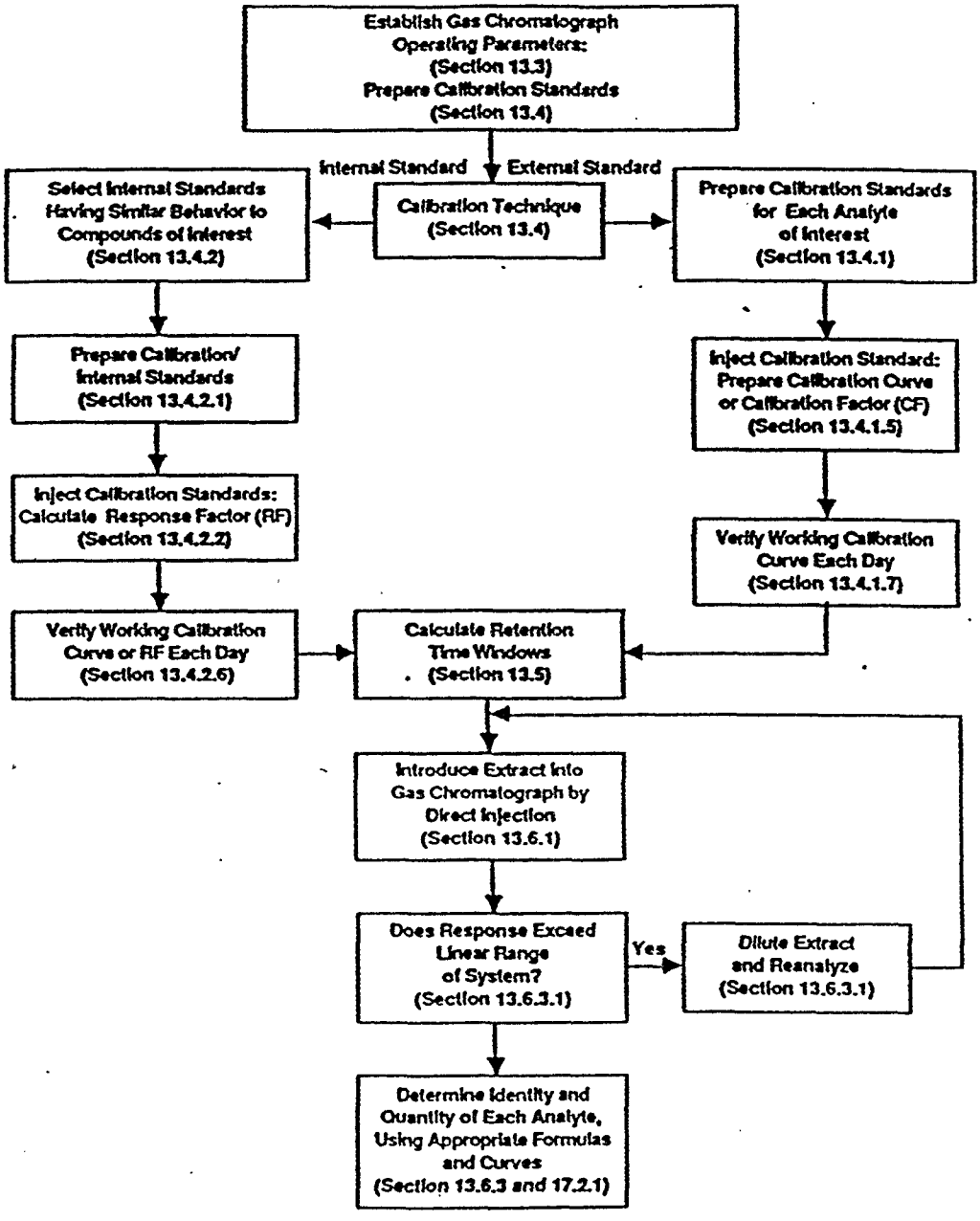
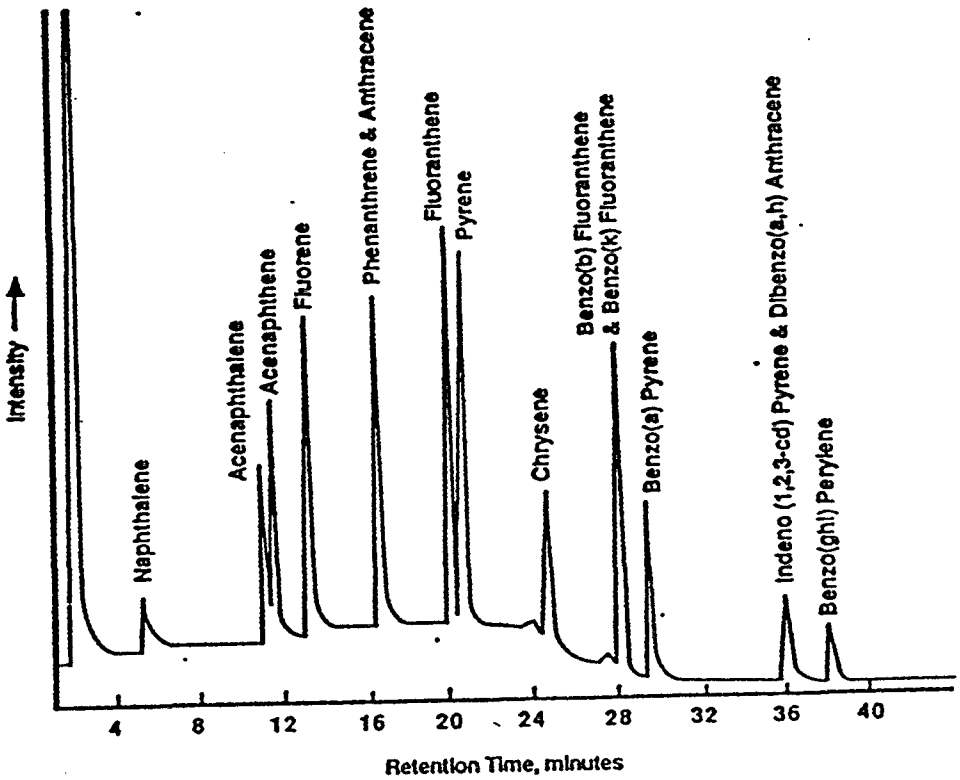


FIGURE 13.0 GC CALIBRATION AND RETENTION TIME WINDOW DETERMINATION.



Column: 3% OV-17 on Chromosorb W-AW-DCMS
Program: 100 °C. 4 min., 8 ° per min. to 280 °C.
Detector: Flame Ionization

FIGURE 14.0 TYPICAL CHROMATOGRAM OF SELECTIVE PNAs BY GC EQUIPPED WITH FI DETECTOR.

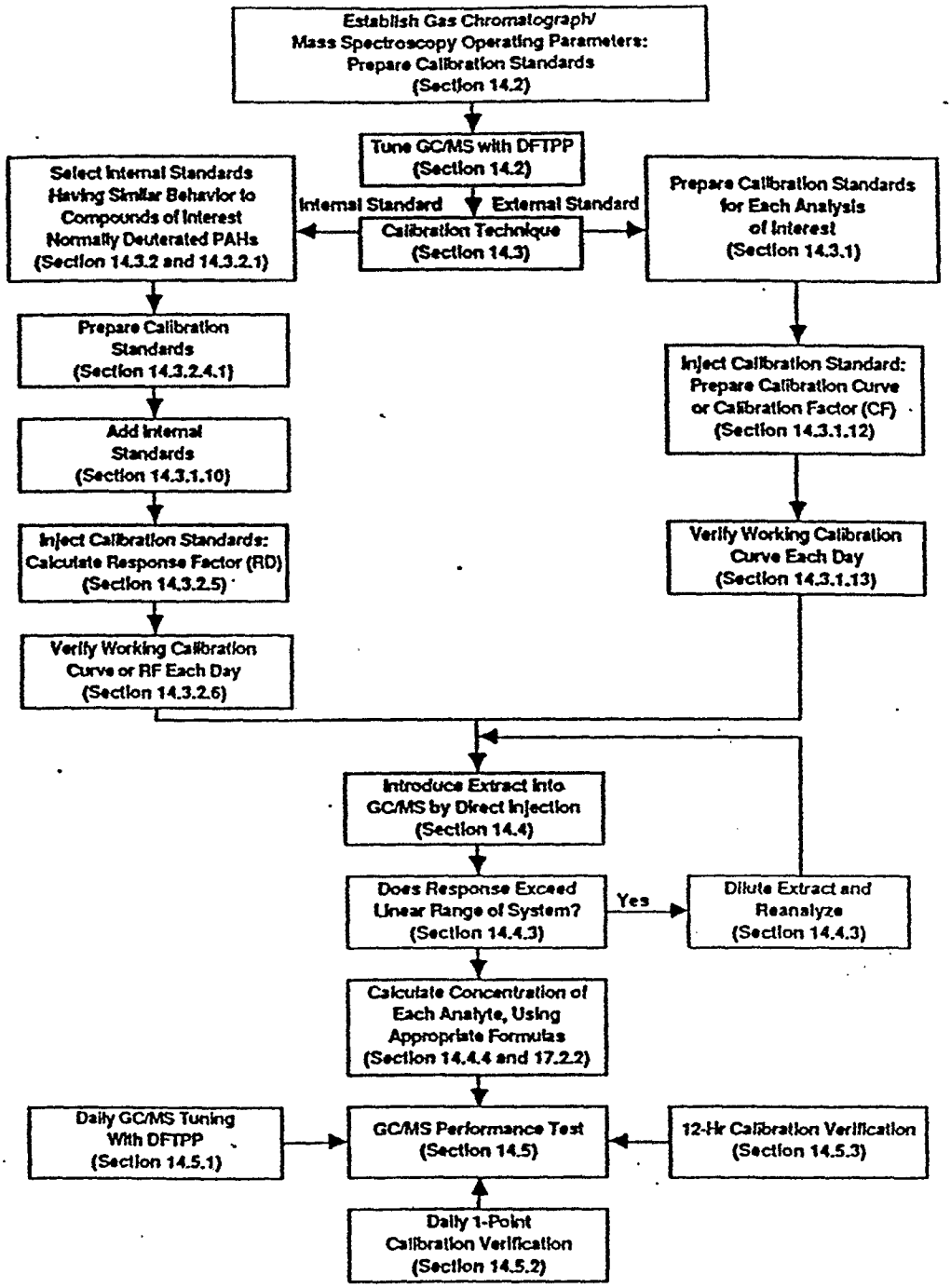


FIGURE 15.0 GC/MS CALIBRATION AND ANALYSIS.

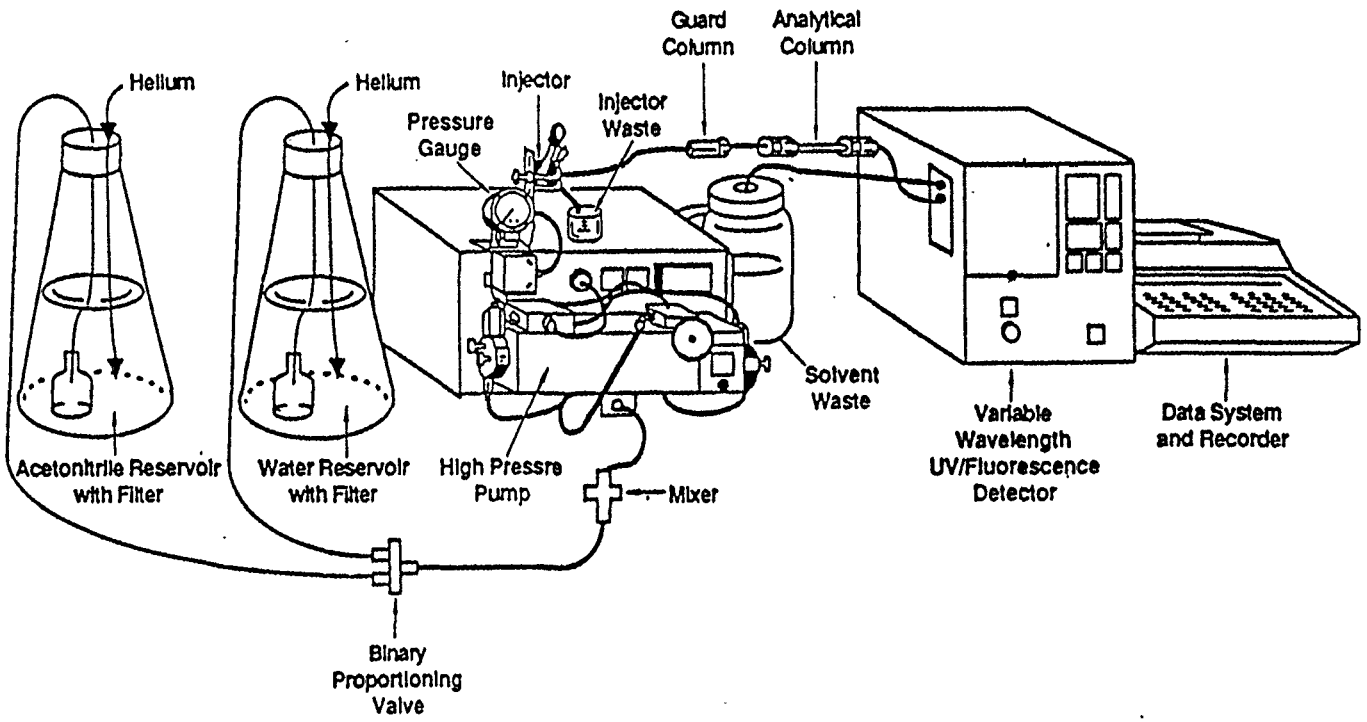


FIGURE 16. IMPORTANT COMPONENTS OF AN HPLC SYSTEM.

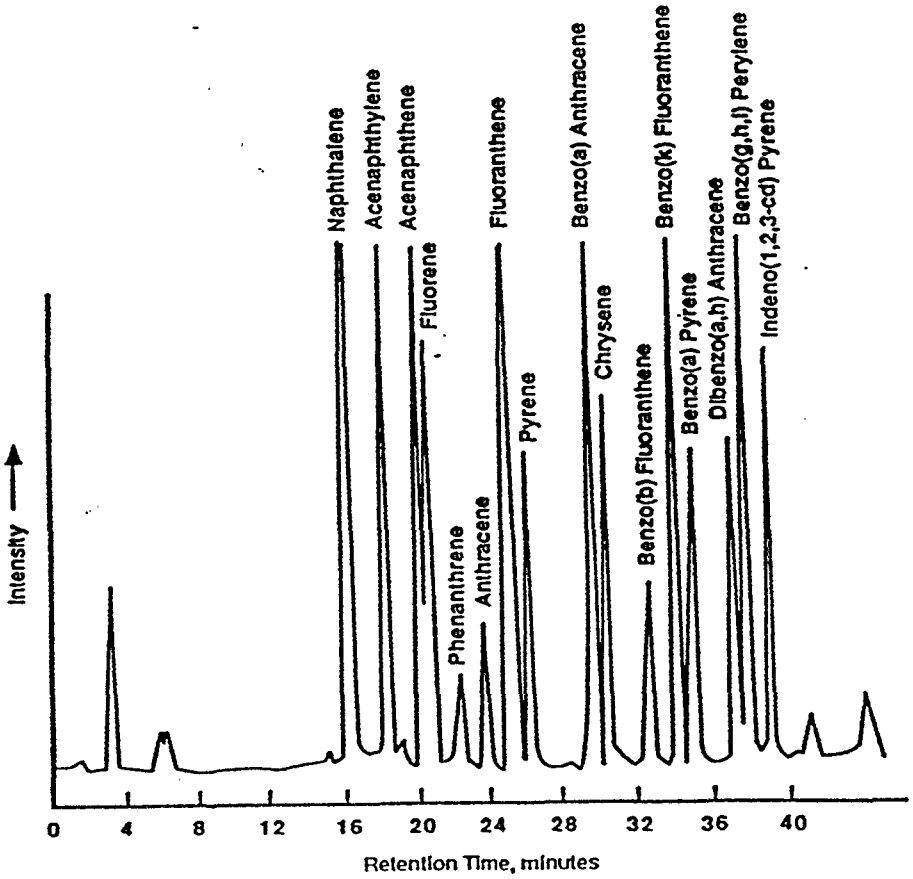


FIGURE 17.0 TYPICAL CHROMATOGRAM OF SELECTIVE PAHs ASSOCIATES WITH HPLC ANALYSIS WITH FLUORESCENCE DETECTION.

METHOD TO4

Revision 1.0
April, 1984

METHOD FOR THE DETERMINATION OF ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN AMBIENT AIR

1. Scope

1.1 This document describes a method for determination of a variety of organochlorine pesticides and polychlorinated biphenyls (PCBs) in ambient air. Generally, detection limits of >1 ng/m^3 are achievable using a 24-hour sampling period.

1.2 Specific compounds for which the method has been employed are listed in Table 1. Several references are available which provide further details on the development and application of the method. The sample cleanup and analysis methods are identical to those described in U. S. EPA Method 608. That method is included as Appendix A of this methods compendium.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition of Terms Related to Atmospheric Sampling and Analysis (7).

2.2 Other Documents

Ambient Air Studies (1-3)

U. S. EPA Technical Assistance Document (4).

U. S. EPA Method 608 (5). See Appendix A of methods compendium.

3. Summary of Method

3.1 A modified high volume sampler consisting of a glass fiber filter with a polyurethane foam (PUF) backup absorbent cartridge is used to sample ambient air at a rate of ∿200-280 L/minute.

3.2 The filter and PUF cartridge are placed in clean, sealed containers and returned to the laboratory for analysis. The PCBs and pesticides are recovered by Soxhlet extraction with 5% ether in hexane.

3.3 The extracts are reduced in volume using Kuderna-Danish (K-D) concentration techniques and subjected to column chromatographic cleanup.

3.4 The extracts are analyzed for pesticides and PCBs using gas chromatography with electron capture detection (GC-ECD), as described in U. S. EPA Method 608 (5).

4. Significance

4.1 Pesticides, particularly organochlorine pesticides, are widely used in both rural and urban areas for a variety of applications. PCBs are less widely used, due to extensive restrictions placed on their manufacture. However, human exposure to PCBs continues to be a problem because of their presence in various electrical products.

4.2 Many pesticides and PCBs exhibit bioaccumulative, chronic health effects and hence monitoring ambient air for such compounds is of great importance.

4.3 The relatively low levels of such compounds in the environment requires the use of high volume sampling techniques to acquire sufficient sample for analysis. However, the volatility of these compounds prevents efficient collection on filter media. Consequently, this method utilizes both a filter and a PUF backup cartridge which provides for efficient collection of most organochlorine pesticides, PCBs, and many other organics within the same volatility range.

5. Definitions

Definitions used in this document and any user-prepared SOPs should be consistent with ASTM D1356 (7). All abbreviations

and symbols are defined within this document at the point of use.

6. Interferences

6.1 The use of column chromatographic cleanup and selective GC detection (GC-ECD) minimizes the risk of interference from extraneous organic compounds. However, the fact that PCBs as well as certain organochlorine pesticides (e.g. toxaphene and chlordane) are complex mixtures of individual compounds can cause difficulty in accurately quantifying a particular formulation in a multiple component mixture.

6.2 Contamination of glassware and sampling apparatus with traces of pesticides or PCBs can be a major source of error in the method, particularly when sampling near high level sources (e.g. dumpsites, waste processing plants, etc.) careful attention to cleaning and handling procedures is required in all steps of the sampling and analysis to minimize this source of error.

7. Apparatus

7.1 Hi-Vol Sampler with PUF cartridge - available from General Metal Works (Model PS-1). See Figure 1.

7.2 Sampling Head to contain glass cartridge with PUF plug - available from General Metal Works. See Figure 2.

7.3 Calibration orifice - available from General Metal Works.

7.4 Manometer - to use with calibration orifice.

7.5 Soxhlet extraction system - including Soxhlet extractors (500 and 250 mL), heating mantels, variable voltage transformers, and cooling water source - for extraction of PUF cartridges before and after sampling. Also for extraction of filter samples.

7.6 Vacuum oven connected to water aspirator - for drying extracted PUF cartridges.

7.7 Gas chromatograph with electron capture detector - (consult U. S. EPA Method 608 for specifications).

7.8 Forceps - to handle quartz fiber filter samples.

7.9 Die - to cut PUF plugs.

7.10 Various items for extract preparation, cleanup, and analysis - consult U. S. EPA Method 608 for detailed listing.

7.11 Chromatography column - 2 mm I.D. x 15 cm long - for alumina cleanup.

8. Reagent and Materials

8.1 Polyurethane foam - 3 inch thick sheet stock, polyether type used in furniture upholstering. Density 0.022 g/cm^3.

8.2 Polyester gloves - for handling PUF cartridges and filters

8.3 Filters, quartz fiber - Pallflex 2500 QAST , or equivalent.

8.4 Wool felt filter - 4.9 mg/cm^2 and 0.6 mm thick. To fit sample head for collection efficiency studies. Pre-extracted with 5% diethyl ether in hexane.

8.5 Hexane - Pesticide or distilled in glass grade.

8.6 Diethyl ether - preserved with 2% ethanol - distilled in glass grade, or equivalent.

8.7 Acetone - Pesticide or distilled in glass grade,

8.8 Glass container for PUF cartridges.

8.9 Glass petri dish - for shipment of filters to and from the laboratory.

8.10 Ice chest - to store samples at ~0°C after collection.

8.11 Various materials needed for extract preparation, cleanup, and analysis - consult U. S. EPA Method 608 for details (Appendix A of this compendium).

8.12 Alumina - activity grade IV. 100/200 mesh

9. Assembly and Calibration of Sampling Apparatus

9.1 Description of Sampling Apparatus

9.1.1 The entire sampling system is diagrammed in Figure 1. This sampler was developed by Syracuse University

Research Corporation (SURC) under a U. S. EPA contract (6) and further modified by Southwest Research Institute and the U. S. EPA. A unit specifically designed for this method is now commercially available (Model PS-1 - General Metal Works, Inc., Village of Cleves, Ohio). The method writeup assumes the use of the commercial device, although the earlier modified device is also considered acceptable.

9.1.2 The sampling module (Figure 2) consists of a glass sampling cartridge and an air-tight metal cartridge holder. The PUF plug is retained in the glass sampling cartridge.

9.2 Calibration of Sampling System

9.2.1 The airflow through the sampling system is monitored by a venturi/Manehelic assembly, as shown in Figure 1. A multipoint calibration of the venturi/magnehelic assembly must be conducted every six months using an audit calibration orifice, as described in the U. S. EPA High Volume Sampling Method (8). A single point calibration must be performed before and after each sample collection, using the procedure described below.

9.2.2 Prior to calibration a "dummy" PUF cartridge and filter are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow rate corresponding to ∿110% of the desired flow rate is indicated on the magnehelic (based on the previously obtained multipoint calibration curve). The motor is allowed to warmup for ∿10 minutes and then the flow control valve is adjusted to achieve the desired flow rate. The ambient temperature and barometric pressure should

be recorded on an appropriate data sheet (e.g. Figure 3).

9.2.3 The calibration orifice is then placed on the sampling head and a manometer is attached to the tap on the calibration orifice. The sampler is momentarily turned off to set the zero level of the manometer. The sampler is then switched on and the manometer reading is recorded, once a stable reading is achieved. The sampler is then shut off.

9.2.4 The calibration curve for the orifice is used to calculate sample flow from the data obtained in 9.2.3, and the calibration curve for the venturi/ magnehelic assembly is used to calculate sample flow from the data obtained in 9.2.2. The calibration data should be recorded on an appropriate data sheet (e.g. Figure 3). If the two values do not agree within 10% the sampler should be inspected for damage, flow blockage, etc. If no obvious problems are found the sampler should be recalibrated (multipoint) according to the U. S. EPA High Volume Sampling procedure (8).

9.2.5 A multipoint calibration of the calibration orifice, against a primary standard, should be obtained annually.

10. Preparation of Sampling (PUF) Cartridges

10.1 The PUF adsorbent is a polyether-type polyurethane foam (density No. 3014 or 0.0225 g/cm^3). This type of foam is used for furniture upholstery. It is white and yellows on exposure to light.

10.2 The PUF inserts are 6.0 cm diameter cylindrical plugs cut from 3 inch sheet stock and should fit with slight compression in the glass cartridge, supported by the wire

screen. See Figure 2. During cutting the die is rotated at high speed (e.g. in a drill press) and continuously lubricated with water.

10.3 For initial cleanup the PUF plug is placed in a Soxhlet extractor and extracted with acetone for 14-24 hours at approximately 4 cycles per hour. When cartridges are reused, 5% diethyl ether in n-hexane can be used as the cleanup solvent.

10.4 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).

10.5 The PUF is placed into the glass sampling cartridge using polyester gloves. The module is wrapped with hexane rinsed aluminum foil, placed in a labeled container and tightly sealed.

10.6 Other adsorbents may be suitable for this method as indicated in the various references (1-3). If such materials are employed the user must define appropriate preparation procedures based on the information contained in these references.

10.7 At least one assembled cartridge from each batch must be analyzed, as a laboratory blank, using the procedures described in Section 12, before the batch is considered acceptable for field use. A blank level of <10 ng/plug for single compounds is considered to be acceptable. For multiple component mixtures (e.g. Arochlors) the blank level should be <100 ng/plug.

11. Sampling

11.1 After the sampling system has been assembled and calibrated as described in Section 9 it can be used to collect air samples as described below.

11.2 The samples should be located in an unobstructed area, at least two meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind

direction to prevent recycling of air.

11.3 A clean sampling cartridge and quartz fiber filter are removed from sealed transport containers and placed in the sampling head using forceps and gloved hands. The head is tightly sealed into the sampling system. The aluminum foil wrapping is placed back in the sealed container for later use.

11.4 The zero reading of the Magnehelic is checked. Ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number and PUF cartridge number are recorded. A suitable data sheet is shown in Figure 4.

11.5 The voltage variator and flow control valve are placed at the settings used in 9.2.3 and the power switch is turned on. The elapsed time meter is activated and the start time recorded. The flow (Magnehelic setting) is adjusted, if necessary using the flow control valve.

11.6 The Magnehelic reading is recorded every six hours during the sampling period. The calibration curve (Section 9.2.7) is used to calculate the flow rate. Ambient temperature and barometric pressure are recorded at the beginning and end of the sampling period.

11.7 At the end of the desired sampling period the power is turned off and the filter and PUF cartridges are wrapped with the original aluminum foil and placed in sealed, labeled containers for transport back to the laboratory.

11.8 The Magnehelic calibration is checked using the calibration orifice as described in Section 9.2.4. If the calibration deviates by more than 10% from the initial reading the flow data for that sample must be marked as suspect and the sampler should be inspected and/or removed from service.

11.9 At least one field blank will be returned to the laboratory with each group of samples. A field blank is treated exactly as a sample except that no air is drawn through the cartridge.

11.10 Samples are stored at ∿20°C in an ice chest until receipt at the analytical laboratory, at which time they are stored refrigerated at 4°C.

12. Sample Preparation and Analysis

12.1 Sample Preparation

12.1.1 All samples should be extracted within 1 week after collection.

12.1.2 PUF cartridges are removed from the sealed con-container using gloved hands, the aluminum foil wrapping is removed, and the cartridges are placed into a 500-mL Soxhlet extraction. The cartridges are extracted for 14-24 hours at ∿4 cycles/hour with 5% diethyl ether in hexane. Extracted cartridges can be dried and reused following the handling procedures in Section 10. The quartz filter can be placed in the extractor with the PUF cartridges. However, if separate analysis is desired then one can proceed with 12.1.3.

12.1.3 If separate analysis is desired, quartz filters are placed in a 250-mL Soxhlet extractor and extracted for 14-24 hours with 5% diethyl ether in hexane.

12.1.4 The extracts are concentrated to 10 mL final volume using 500-mL Kuderna-Danish concentrators as described in EPA Method 608 (5), using a hot water bath. The concentrated extracts are stored refrigerated in sealed 4-dram vials having teflon-lined screw-caps until analyzed or subjected to cleanup.

12.2 Sample Cleanup

12.2.1 If only organochlorine pesticides and PCBs are sought, an alumina cleanup procedure reported in the literature is appropriate (1). Prior to cleanup the sample

extract is carefully reduced to 1 mL using a gentle steam of clean nitrogen.

12.2.2 A glass chromatographic column (2 mm ID x 15 cm long) is packed with alumina, activity grade IV and rinsed with ~20 mL of n-hexane. The concentrated sample extract (from 12.2.1) is placed on the column and eluted with 10 mL of n-hexane at a rate of 0.5 mL/minute. The eluate volume is adjusted to exactly 10 mL and analyzed as described in 12.3.

12.2.3 If other pesticides are sought, alternate cleanup procedures (e.g. Florisil) may be required. Method 608 (5) identifies appropriate cleanup procedures.

12.3 Sample Analysis

12.3.1 Sample analysis is performed using GC/ECD as described in EPA Method 608 (5). The user must consult this method for detailed analytical procedures.

12.3.2 GC retention times and conditions are identified in Table 1 for the compounds of interest.

13. GC Calibration

Appropriate calibration procedures are identified in EPA Method 608 (5).

14. Calculations

14.1 The total sample volume (V_m) is calculated from the periodic flow readings (Magnehelic) taken in Section 11.6 using the following equation.

$$V_m = \frac{Q_1 + Q_2 \ldots Q_N}{N} X \frac{T}{1000}$$

where

V_m = Total sample volume (m^3).

Q_1, $Q_2 \ldots Q_N$ = Flow rates determined at the beginning, end, and intermediate points during sampling (L/minute).

N = Number of data points averaged.

T = Elapsed sampling time (minutes).

14.2 The volume of air sampled can be converted to standard conditions (760 mm Hg pressure and 25°C) using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273+t_A}$$

where

V_s = Total sample volume at 25°C and 760 mm Hg pressure (m^3)

V_m = Total sample flow under ambient conditions (m^3)

P_A = Ambient pressure (mm Hg)

t_A = Ambient temperature (°C)

14.3 The concentration of compound in the sample is calculated using the following equation:

$$C_A = \frac{A \times V_E}{V_i \times V_s}$$

where

C_A = Concentration of analyte in the sample, $\mu g/m^3$

A = Calculated amount of material injected onto the chromatograph based on calibration curve for injected standards (nanograms)

V_i = Volume of extract injected (µL).

V_E = Final volume of extract (mL).
V_s = Total volume of air samples corrected to standard conditions (m^3).

14. Performance Criteria and Quality Assurance

This section summarizes the quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory.

14.1 Standard Operating Procedures (SOPs)

14.1.1 Users should generate SOPs describing the following activities as accomplished in their laboratory: 1) assembly, calibration and operation of the sampling system, 2) preparation, purification, storage and handling of sampling cartridges, 3) assembly, calibration and operation of the GC/ECD system, and 4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

14.2 Process, Field, and Solvent Blanks

14.2.1 One PUF cartridge and filter from each batch of approximately twenty should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank.

14.2.2 During each sampling episode at least one PUF cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

14.2.3 During the analysis of each batch of samples at least one solvent process blank (all steps conducted but no PUF cartridge or filter included) should be

carried through the procedure and analyzed.

14.2.4 Blank levels should not exceed ~10 ng/sample for single components or ~100 ng/sample for multiple component mixtures (e.g. PCBs).

14.3 Collection Efficiency and Spike Recovery

14.3.1 Before using the method for sample analysis each laboratory must determine their collection efficiency for the components of interest.

14.3.2 The glass fiber filter in the sampler is replaced with a hexane-extracted wool felt filter (weight 14.9 mg/cm^2, 0.6 mm thick). The filter is spiked with microgram amounts of the compounds of interest by dropwise addition of hexane solutions of the compounds. The solvent is allowed to evaporate and filter is placed into the sampling system for immediate use.

14.3.3 The sampling system, including a clean PUF cartridge, is activated and set at the desired sampling flow rate. The sample flow is monitored for 24 hours.

14.3.4 The filter and PUF cartridge are then removed and analyzed as described in Section 12.

14.3.5 A second sample, unspiked is collected over the same time period to account for any background levels of components in the ambient air matrix.

14.3.6 A third PUF cartridge is spiked with the same amounts of the compounds used in 14.3.2 and extracted to determine analytical recovery.

14.3.7 In general analytical recoveries and collection efficiencies of 75% are considered to be acceptable method performance.

14.3.8 Replicate (at least triplicate) determinations of collection efficiency should be made. Relative standard deviations for these replicate determinations of ± 15% or less is considered acceptable performance.

14.3.9 Blind spiked samples should be included with sample sets periodically, as a check on analytical performance.

14.4 Method Precision and Accuracy

Typical method recovery data are shown in Table 1. Recoveries for the various chlorobiphenyls illustrate the fact that all components of an Arochlor mixture will not be retained to the same extent. Recoveries for tetrachlorobiphenyls and above are generally greater than 85% but di- and trichloro homologs may not be recovered quantitatively.

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8. Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method). Federal Register, Sept. 14, 1972 or 40CFR50 Appendix B.

TABLE 1. SELECTED COMPONENTS DETERMINED USING HI-VOL/PUF SAMPLING PROCEDURE

Compound	GC Retention Time, Minutes[a]	24-Hour Sampling Efficiency[b] Air Concentration ng/m^3	24-Hour Sampling Efficiency[b] % Recovery
Aldrin	2.4	0.3-3.0	28
4,4'-DDE	5.1	0.6-6.0	89
4,4'-DDT	9.4	1.8-18	83
Chlordane	(c)	15-150	73
Chlorobiphenyls			
4,4' Di-	--	2.0-20	62
2,4,5 Tri-	---	0.2-2.0	36
2,4',5 Tri-	--	0.2-2.0	86
2,2',5,5' Tetra-	--	0.2-2.0	94
2,2',4,5,5' Penta-	--	0.2-2.0	92
2,2',4,4',5,5' Hexa	--	0.2-2.0	86

(a) Data from U.S. EPA Method 608. Conditions are as follows:

Stationary Phase - 1.5% SP2250/1.95% SP-2401 on Supelcoport (100/120 mesh) packed in 1.8 mm long x 4 mm ID glass column.

Carrier - 5/95 methane/Argon at 60 mL/Minute

Column Temperature - 160°C except for PCBs which are determined at 200°C.

(b) From Reference 2.

(c) Multiple component formulation. See U.S. EPA Method 608.

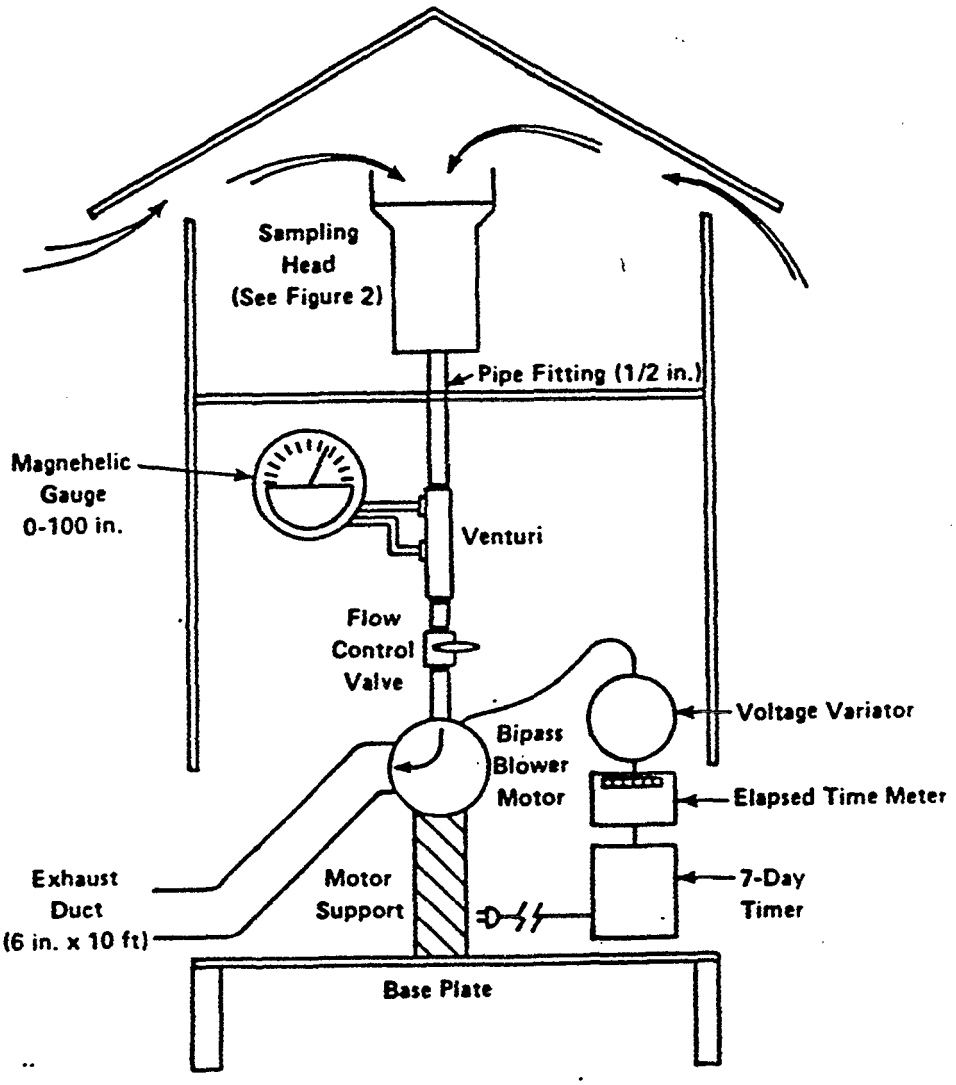

FIGURE 1. HIGH VOLUME AIR SAMPLER. AVAILABLE FROM GENERAL METAL WORKS (MODEL PS-1)

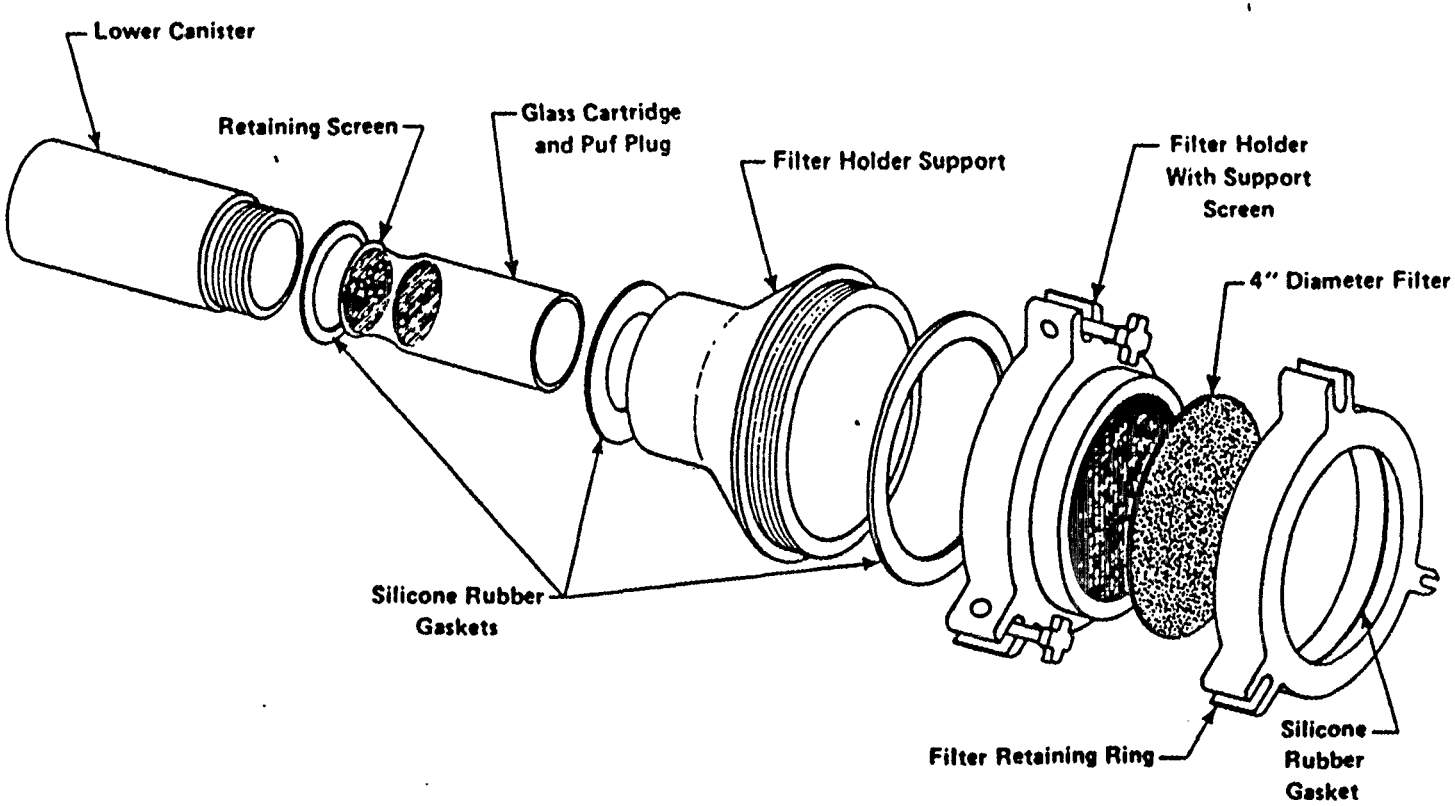

FIGURE 2. SAMPLING HEAD

Performed by_____ Calibration Orifice S/N_____ Ambient Temperature_____°C

Date/Time_____ Manometer S/N _____ Bar.Press. _____ mm Hg

Sampler S/N	Variac Setting V	Timer OK? Yes/No	Calibration Orifice Data		Sampler Venturi Data		% Difference Between Calibration and Sample Venturi Flow Rates	Comments
			Manometer, in. H_2O	Flow Rate, scm /min[a]	Magnehelic, in. H_2O	Flow Rate scm/min [b]		

(a) From Calibration Tables for Calibration Orifice or Venturi Tube

(b) From Calibration Tables for Venturi Tube in each Hi-Vol unit. Date check by_____ Date_____

FIGURE 3. TYPICAL CALIBRATION SHEET FOR HIGH VOLUME SAMPLER

Site _____ Date _____ Performed by _____

Sampler S/N	Sampling Location I.D.	New Filter (√)	PUF Cart. No.	Variac Setting	Clock Time			Sampler Timer			Venturi Readings: Time/Magnahelic in. H_2O				Ambient Temperature, °C		Barometric Pressure, mm Hg		Comments
					Start, hr CDT	Stop, hr CDT	Min Elapsed	Start, min	Stop, min	Min Elapsed	1	2	3	4	Start	Stop	Start	Stop	

(a) Record any evidence of tampering with sampler and/or abnormalities in sampler operation, PUF cartridge condition or handling, etc.

Data Checked By _____ Date _____

T04-20

FIGURE 4. TYPICAL SAMPLING DATA FORM FOR HIGH VOLUME PESTICIDE/PCB SAMPLER

APPENDIX E

DERIVATION OF AIR ACTION LEVELS

APPENDIX E

DERIVATION OF AIR ACTION LEVELS

Combustion, Inc. Site Removal Action
Livingston Parish, Louisiana

The air action levels during performance of the Removal Action at the Combustion, Inc. site, presented herein, were developed in accordance with the Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual (Part A) and Human Health Evaluation Manual, Supplemental Guidance: "Standard Default Exposure Factors" (OSWER Directive 9285.6-03). Health-based criteria, inhalation unit risk values and subchronic reference concentrations, were obtained from the Integrated Risk Information System (IRIS), and the 1991 and 1992 Health Effects Assessment Summary Tables (HEAST).

Carcinogenic Health Effects

The air action levels were developed with the assumption that the active remediation would occur over a two-year period. The inhalation unit risk values were prorated to account for the duration of the active remediation (The Risk Assessment Guidelines of 1986). The exposure duration was adjusted from a 70 year exposure to a two year exposure. Unit risk values are used with the assumption of one excess cancer case per one hundred thousand individuals.

Air action levels for carcinogenic health effects correspond to the average concentration of each specific constituent over the entire exposure period at each receptor location. For ease of data handling and reporting, all downwind data will be pooled to determine average concentrations of each constituent. Wind direction is accounted for by applying a wind direction factor of 0.5 (i.e., any receptor is downwind of the site less than 50% of the time). A summary of wind direction recordings for a nine year period is provided in Table E-1. The 50% value is derived by grouping three adjacent vectors (example: north, northeast and east) for each season and identifying the maximum value. The maximum observed wind direction is for the northeast, east and southeast for a total of 48% of the time (this value is rounded to 50%).

TABLE E-1

BATON ROUGE WIND ROSE SUMMARY[a]

Combustion, Inc. Site
Denham Springs, Louisiana

Time Deliver[a]	Percentage of Time Wind Blows From a Particular Direction								
	N	NE	E	SE	S	SW	W	NW	Calm
Annual	13.4	11.6	15.9	14.4	12.4	7.0	7.8	8.0	9.3
Spring[b]	11.2	9.8	13.9	16.8	19.7	8.2	6.3	7.4	6.5
Summer[c]	10.1	10.8	14.9	12.1	10.0	10.0	12.8	6.9	12.4
Fall[d]	15.6	14.6	19.5	13.6	7.6	3.5	5.8	7.8	11.6
Winter[e]	17.4	11.5	14.9	14.9	13.0	5.5	6.5	9.8	6.6

NOTES:

[a]Source: Local Climatological Data, 1981, Baton Rouge, Louisiana (NOAA)
[b]March, April, May (1965–1974)
[c]June, July, August (1965–1974)
[d]September, October, November (1965–1974)
[e]December, January, February (1965–1974)

The equation for determination of air action levels is presented in Table E-2. Health-based criteria used in calculation of the air action levels are presented in Table E-3. Calculated air action levels are provided in Table E-4.

Noncarcinogenic Health Effects

The duration of active remediation at the Combustion site is assumed to be two years. This duration of time is within the exposure range of subchronic reference concentration (RfC).

Subchronic RfCs estimate a daily exposure level for human population, including sensitive subpopulations such as children, that is likely to be without adverse effects for an exposure duration of two weeks to seven years. Subchronic RfCs could be used without modification as two-year air action levels for chemicals with noncarcinogenic health effects (Table E-4). Subchronic RfCs are used with the assumption of a hazard index (HI) equal to unity (1).

Polycyclic Aromatic Hydrocarbons

Carcinogenic Polycyclic Aromatic Hydrocarbons (PAHs) should be evaluated on the basis of the toxicity value for benzo(a)pyrene. PAHs can be evaluated as a class of chemicals using the toxicity equivalency factor (TEF) methodology. The following TEFs should be used to convert the concentration of each carcinogenic PAH compound to the relative potency of benzo(a)pyrene.

Compound	TEF
Benzo(a)pyrene	1.0
Benzo(a)anthracene	0.1
Benzo(b)fluoranthene	0.1
Benzo(k)fluoranthene	0.1
Chrysene	0.01
Dibenzo(a,h)anthracene	1.0
Indeno(1,2,3-c,d)pyrene	0.1

TABLE E-2

EQUATION FOR DETERMINATION OF AIR ACTION LEVELS

Combustion, Inc. Site
Denham Springs, Louisiana

$$\text{Air Action Level } (\mu g/M^3) = \frac{TR * AT}{UT * ED * WF} + BG$$

TR = Target Risk (1×10^{-5})

AT = Averaging Time (70 years)

UT = Inhalation Unit Risk Value (See Table 1)

ED = Exposure Durations (Years)

WF = Wind Factor to adjust for maximum seasonal wind direction of 50% (0.5).

BG = Upwind (background) air concentration for measured compound.

TABLE E–3

HEALTH–BASED CRITERIA USED TO CALCULATE
AIR ACTION LEVELS FOR THE COMBUSTION, INC. SITE

Combustion, Inc. Site
Denham Springs, Louisiana

Contaminant	Carcinogenic Group	Inhalation Unit Risk	Subchronic Reference Concentration
Benzene	A	8.3E–6	---
Benzo(a)pyrene	B2	1.7E–4	---
Chlorobenzene	---	---	2E–1
Chloroethane	---	---	1E+1
Chloroform	B2	2.3E–5	---
1,1–Dichloroethane	C	---	5E+0
1,2–Dichloroethane	B2	2.6E–5	---
1,2–Dichloroethene	---	---	---
1,4–Dichlorobenzene	C	---	7E–1
Ethyl benzene	---	---	1E+0
Lead	B2	---	---
Styrene	B2	5.7E–7	---
Tetrachloroethene	B2	5.2E–7	1E–1
Toluene	---	---	2E+0
Trichloroethene	B2	1.7E–6	---
Xylenes (mixed)	---	---	3E–1

NOTE:
Inhalation unit risk values are expressed 1/(μg/cubic meter) and reference concentrations are expressed in mg/cubic meter.

TABLE E-4

ACTION LEVELS FOR SPECIFIC CHEMICALS IN AIR
PHASE I AND PHASE II REMOVAL ACTION

Combustion, Inc. Site
Denham Springs, Louisiana

Parameters		Method Detection Limits ug/m^3 (e)	Action Levels (a)(b)(c) ug/m^3
Benzene	(a)	4	84
Chlorobenzene	(f)	67	200
Chloroethane	(f)	3333	10,000
Chloroform	(a)	2	30
1,1-Dichloroethane	(f)	1667	5000
1,2-Dichloroethane	(a)	1	27
1,2-Dichloroethene	--	50	Monitor Only
1,4-Dichlorobenzene	(f)	233	700
Ethyl benzene	(f)	333	1000
Styrene	(a)	61	1220
Tetrachloroethene	(a)	67	1340
Toluene	(f)	667	2000
Trichloroethene	(a)	21	420
Xylenes	(f)	100	300
PCBs	(h)	0.5	1
PNAs	(a) (d)	0.2	4
Lead	(g)	0.5	1.5

NOTES:

(a) Action levels derived using a 1 x 10^{-5} cancer risk factor for carcinogenic compounds.

(b) Action levels reflect exposure durations adjusted for a maximum seasonal wind direction of 50% (e.g., no one receptor is downwind of the site more than 50% of the time over a one-year period). Therefore, exposure duration equals (project time) X 0.5. Reference Wind Rose charts found in Appendix E.

(c) Actions levels equate to the running average of the downwind data results and not instantaneous or maximum daily readings.

(d) Equivalents to benzo(a)pyrene. See Appendix E for equivalent factors for specific PNAs.

(e) These are the target detection limits but may be modified depending on matrix interference and other laboratory factors.

(f) Action levels derived using non-carcinogenic health effects subchronic reference concentration (RfC) and a Hazard Index of one.

(g) National Ambient Air Quality Standards.

(h) National Institute for Occupational Safety and Health (NIOSH) proposed standard and referenced by EPA Region VI.

Air Action Levels

The carcinogenic and noncarcinogenic health effects of chemicals were assessed in the calculation and determination of the recommended air action levels are provided in Table E-4. The air action levels should be protective of human populations including sensitive individuals living in the vicinity of the Combustion, Inc. site during the Removal Action. The air action levels were adjusted to account for the two years of anticipated remedial activity. The air action levels should be compared to cumulative average air concentrations. Therefore, it may be acceptable to exceed these air action levels on a short term basis without harm to human health.

Local Climatological Data

Annual Summary With Comparative Data

1981

BATON ROUGE, LOUISIANA

Narrative Climatological Summary

Baton Rouge, Louisiana's capital city, is located on the east side of the Mississippi River, in the southeastern section of the state, some 60 to 70 miles inland from the coast. The area is near the first evident relief north of the deltaic coastal plain, marsh and swamp terrain stretching southward to the Gulf of Mexico. The NOAA National Weather Service Office is located at Ryan Airport, some eight miles north of the downtown area. Elevations in East Baton Rouge Parish range from near 25 feet above sea level in southern sections to more than 100 feet in the extreme north.

The general climate of Baton Rouge is humid subtropical, but the city is subject to significant polar influences during winter, as masses of cold air periodically move southward across the plains and the Mississippi Valley, displacing warm moist air. Prevailing wind flow is from a southerly direction during much of the year. This movement of maritime air from the Gulf of Mexico helps to temper extremes of summer heat, to shorten the duration of winter cold spells, and provides a source of abundant moisture and rainfall. Winds are usually rather light. About 80 percent of hourly wind speed observations during the year are 12 m.p.h. or less.

Rainfall is heavy with the normal annual total more than 54 inches. Amounts are substantial in all seasons, although there is an early autumn minimum in September and October. All other months receive an average total of more than four inches. Almost all rainfall is of the convective and air mass types—showery and brief—except occasionally during winter when nearly continuous rains, produced as cold fronts, become stationary in the region and may persist for a few days. Extremes of precipitation may occur in all seasons, and although torrential rainfall is unusual in East Baton Rough Parish, 12.08 inches were reported in 24 hours on April 13-14, 1967, with 11.29 inches of this amount measured in 11 hours.

The winter months are normally mild with cold spells usually of short duration. The typical pattern is weather turning cold with rain one day, reaching the lowest temperatures after sky is clear on the second day, and warming on the third day. Freezing or sub-freezing minimum temperatures occur several times annually, but rarely do maximum temperatures fail to rise above the freezing point. The longest known period during which temperatures remained below 33°F is 71 hours, on January 9-12, 1962. The average date of the first 32°F in the autumn is November 22, and the average date of the last 32°F in spring is February 22. These dates produce a mean freeze-free period of some 273 days. Individual years have from fewer than 10 to more than 30 days with freezing temperature. While temperatures of freezing or below occur each winter, readings drop below 29°F in only about 60 percent of the seasons. Snow is a negligible form of precipitation; total annual snowfall averages only a fraction of an inch and many years pass with no measurable snow. The heaviest snowfall of record, in February 1895, deposited 12.5 inches in Baton Rouge.

The summer months are consistently quite warm, but maximum temperatures rarely exceed 100°F because of the uniform high humidity of the dominant maritime tropical air mass and the moderating effects of cloudiness and the scattered convective showers and thunderstorms which are a primary feature of the weather during these months. Showers normally fall at any place on about one-third of the days in June, July and August, and are present in the area on more than one-half of the days. The resulting point rainfall totals are usually less than one-half inch except on three or four days per month.

Summer relative humidity exceeds 80 percent for about 12 hours per day. High humidity may be experienced at any hour, but occurs mainly at night; 90 percent or more of the hours from late evening to early morning have relative humidity of 80 percent or higher. Readings of 50 percent or less occur about two hours per day, usually during afternoons; from 25 to 40 percent of the mid-afternoon hours have had relative humidity of less than 50 percent.

Temperatures in the spring are usually mild and pleasant and those in autumn from late September to December are generally delightful for outdoor activities.

Thunderstorms occur each month; they are most frequent in July and August with almost one-half of the days in each month reporting thunder. The fewest days with rain are in October. Dry spells of two to three weeks' duration are not uncommon. The longest period without measurable precipitation is 35 days.

Severe local storms, including hailstorms, tornadoes, and local wind storms, have occurred over small areas in all seasons, but are most frequent during the spring months. Large hail of a damaging nature very rarely occurs and tornadoes in this section of Louisiana are unusual. Since 1900, the centers of five hurricanes have passed very near Baton Rouge. The area has also been affected by several other hurricanes and by several tropical storms which did not attain hurricane intensity. Baton Rouge is in the region where a mean recurrence interval of 50 years gives a standardized extreme mile of wind a speed of about 85 m.p.h.

noaa NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION / ENVIRONMENTAL DATA AND INFORMATION SERVICE / NATIONAL CLIMATIC CENTER ASHEVILLE, N.C.

Meteorological Data For The Current Year

Station: BATON ROUGE, LOUISIANA RYAN AIRPORT Standard time used: CENTRAL Latitude: 30° 32' N Longitude: 91° 08' W Elevation (ground): 64 feet Year: 1981
13970

Month	Temperature °F: Averages: Daily maximum	Daily minimum	Monthly	Extremes: Highest	Date	Lowest	Date	Degree days Base 65 °F: Heating	Cooling	Precipitation in inches: Water equivalent: Total	Greatest in 24 hrs.	Date	Snow, ice pellets: Total	Greatest in 24 hrs.	Date	Relative humidity, pct.: Hour 00 (Local time)	Hour 06 (Local time)	Hour 12 (Local time)	Hour 18 (Local time)	Wind: Resultant: Direction	Resultant speed m.p.h.	Average speed m.p.h.	Fastest mile: Speed m.p.h.	Direction	Date	Percent of possible sunshine	Average sky cover, tenths, sunrise to sunset	Number of days: Sunrise to sunset: Clear	Partly cloudy	Cloudy	Precipitation .01 inch or more	Snow, ice pellets 1.0 inch or more	Thunderstorms	Heavy fog, visibility ¼ mile or less	Temperature °F: Maximum (b): 90° and above	32° and below	Minimum: 32° and below	0° and below	Average station pressure mb: Elev. 76 feet m.s.l.
JAN	57.6	34.7	46.2	75	29	18	13	576	0	1.20	0.68	6	T	T	19	78	83	83	87	01	1.7	5.0	20	09	20		5.1	12	8	11					0	12	0	1020.7
FEB	63.0	42.5	52.8	80	27	21	12	345	7	7.07	3.29	5-6	T	T	13	80	86	81	81	36	0.8	7.1	29	32	11		7.2	9	7	16	1	0			0	4	0	1019.6
MAR	70.9	47.3	59.1	86	31	27	24	192	17	1.74	0.78	4	0.0	0.0		74	85	69	53	03	0.1	7.7	29	21	22		6.8	7	11	13	5	0	0		0	0	0	1019.4
APR	82.1	61.8	72.0	88	30	46	6	10	227	3.09	1.05	23	0.0	0.0		93	95	68	65	15	3.2	5.8	23	33	30		7.4	3	4	18	7	0	0		0	0	0	1017.4
MAY	81.9	61.8	71.9	92	29	50	21	6	226	4.47	2.67	4-5	0.0	0.0		92	92	65	69	13	1.3	6.5	18	19	25		6.5	7	6	18	7	0	0		0	0	0	1011.5
JUN	90.2	73.2	81.7	94	22	68	1	0	509	4.78	1.66	10-11	0.0	0.0		92	95	65	72	17	2.9	5.8	21	08	11		6.1	5	10	8	14	0	10		22	0	0	1013.2
JUL	92.4	74.7	83.6	98	23	70	11	0	581	4.25	1.55	1-2	0.0	0.0		90	94	64	70	23	1.8	4.7	18	28	9		5.8	13	11	7	9	0	13		26	0	0	1014.4
AUG	92.2	73.0	82.6	97	1	69	26	8	553	4.46	1.97	5	0.0	0.0		93	97	61	70	10	0.2	3.9	21	14	30		5.3	7	17	7	7	0	10		26	0	0	1013.2
SEP	87.2	65.4	76.3	92	6	49	19	4	350	3.95	1.95	12-13	0.0	0.0		95	98	58	67	05	1.7	5.5	23	26	24		3.9	16	9	5	5	0	8		12	0	0	1014.9
OCT	79.0	57.6	68.4	91	1	39	28	64	176	1.42	0.62	25-26	0.0	0.0		84	89	62	68	07	3.2	6.9	18	02	23		6.2	8	11	12	9	0	2		2	0	0	1016.3
NOV	74.6	49.6	62.2	85	19	30	21	332	56	1.51	0.76	8-9	0.0	0.0		87	90	55	66	08	0.9	6.8	21	16	30		5.6	10	8	12	9	0	2		2	0	0	1016.3
DEC	61.6	41.9	51.8	77	6	21	19	910	4	5.35	1.74	24	0.0	0.0		76	80	68	65	05	2.6	7.9	22	35	31		5.7	12	4	15	12	0	1		4	0	0	1017.3
YEAR	77.7	57.0	67.4	98	JUL 23	18	JAN 13	1739	2706	43.21	3.29	FEB 5-6	T	T	FEB 13	86	91	59	65	09	0.9	6.2	29	21	MAR 22		5.8	103	122	148	101	0	56	20	91	0	22	0	1015.8

Normals, Means, And Extremes

Month	Temperatures °F: Normal: Daily maximum	Daily minimum	Monthly	Extremes: Record highest	Year	Record lowest	Year	Normal Degree days Base 65 °F: Heating	Cooling	Precipitation in inches: Water equivalent: Normal	Maximum monthly	Year	Minimum monthly	Year	Maximum in 24 hrs.	Year	Snow, ice pellets: Maximum monthly	Year	Maximum in 24 hrs.	Year	Relative humidity pct.: Hour 00 (Local time)	Hour 06 (Local time)	Hour 12 (Local time)	Hour 18 (Local time)	Wind: Mean speed m.p.h.	Prevailing direction	Fastest mile: Speed m.p.h.	Direction	Year	Pct. of possible sunshine	Mean sky cover, tenths, sunrise to sunset	Mean number of days: Sunrise to sunset: Clear	Partly cloudy	Cloudy	Precipitation .01 inch or more	Snow, ice pellets 1.0 inch or more	Thunderstorms	Heavy fog, visibility ¼ mile or less	Temperatures °F Max. (b): 90° and above	32° and below	Min.: 32° and below	0° and below	Average station pressure mb: Elev. 76 feet m.s.l.
(a)				31		31					31		31				11		31		22	22	22	22	38	12	19	19		38	30	30	30	30	30	30	30	22	22	22	22	9
J	61.5	40.5	51.0	82	1957	19	1962	451	17	4.48	9.93	1966	1.15	1971	4.04	1935	0.6	1973	0.6	1973	81	85	66	69	9.1	N	35	23	1975		8.9	7	6	18	0	1	0	10	0	1018.7
F	64.5	43.2	53.9	85	1962	20	1958	335	24	4.74	14.51	1966	0.70	1962	4.72	1979	1.6	1973	1.6	1973	78	84	58	66	9.5	NE	35	26	1978		8.9	6	6	15	0	1	0	6	0	1018.0
M	70.6	48.7	59.7	91	1963	26	1980	208	46	5.14	12.73	1973	0.54	1955	6.07	1973	T	1980	T	1980	68	85	57	59	9.6	NE	35	13	1968		8.6	7	8	16	0	1	0	2	0	1016.2
A	79.0	57.7	68.4	92	1952	37	1975	33	135	5.10	14.84	1980	0.18	1976	12.09	1967	0.0		0.0		83	89	56	59	8.9	SE	35	25	1969		8.2	7	8	15	0	1	0	3	0	1014.5
M	85.2	64.3	74.8	98	1953	44	1954	0	304	4.39	10.70	1953	0.63	1963	4.96	1954	0.0		0.0		84	90	57	61	7.8	SE	48	17	1967		7.8	8	12	11	0	0	0	1	0	1011.6
J	90.3	70.3	80.3	103	1954	55	1972	0	459	3.77	11.36	1962	0.12	1979	3.96	1962	0.0		0.0		85	91	58	63	6.7	SE	40	03	1969		8.5	6	10	8	4	1	2	0	0	1013.7
J	91.2	72.7	82.0	101	1960	59	1969	0	527	4.51	18.94	1963	2.95	1962	9.26	1969	0.0		0.0		87	91	63	70	6.8	S	41	03	1980		8.3	5	15	11	15	0	15	2	24	0	0	0	1014.3
A	91.1	72.1	81.6	102	1962	59	1967	0	515	4.67	13.31	1977	1.32	1980	3.84	1953	0.0		0.0		88	92	63	71	5.6	E	37	32	1975		8.4	7	15	9	12	0	12	2	22	0	0	0	1014.4
S	87.2	67.7	77.5	97	1963	43	1967	0	375	3.79	13.95	1977	0.09	1953	6.31	1973	0.0		0.0		84	91	61	71	6.8	NE	58	06	1965		8.6	9	11	10	5	0	3	1	11	0	0	0	1013.2
O	80.4	56.6	68.5	94	1952	32	1957	54	163	2.65	9.46	1964	T	1978	8.34	1969					85	88	54	65	6.7	NE	48	33	1964		8.3	15	8	8	0	0	0	0	2	0	0	0	1016.3
N	70.3	46.9	58.6	86	1971	21	1976	208	16	3.44	10.35	1977	0.25	1967	4.67	1973	T	1976	T	1976	85	88	58	66	7.8	N	31	22	1977		8.6	10	8	12	2	0	3	0	3	0	0	0	1017.3
D	63.7	42.0	52.9	83	1978	11	1962	381	6	5.83	13.23	1953	1.94	1978	4.12	1953	T	1973	T	1973	82	86	62	68	8.5	SE	38	16	1966		8.2	9	7	15	10	0	9	0	7	0	0	0	1018.2
YR	77.9	56.9	67.4	103	JUN 1954	10	JAN 1962	1670	2585	54.05	14.84	APR 1980	T	OCT 1978	12.09	APR 1967	1.6	FEB 1973	1.6	FEB 1973	84	88	59	65	7.9	SE	58	06	SEP 1965		8.4	101	119	145	100	4	69	36	89	4	26	0	1015.4

Means and extremes above are from existing and comparable exposures. Annual extremes have been exceeded at other sites in the locality as follows: Highest temperature 110 in August 1909; lowest temperature 2 in February 1899; maximum monthly precipitation 23.73 in May 1907; minimum monthly precipitation 0.00 in September 1924.

(a) Length of record, years, through the current year unless otherwise noted, based on January data.
(b) 70° and above at Alaskan stations.
* Less than one half.
T Trace.

NORMALS - Based on record for the 1941-1970 period.
DATE OF AN EXTREME - The most recent in cases of multiple occurrence.
PREVAILING WIND DIRECTION - Record through 1963.
WIND DIRECTION - Numerals indicate tens of degrees clockwise from true north. 00 indicates calm.
FASTEST MILE WIND - Speed is fastest observed 1-minute value when the direction is in tens of degrees.

BATON ROUGE, LA

Average Temperature

Year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	Annual
1942	46.6	51.4	59.5	67.7	74.7	80.4	82.7	82.8	76.0	70.4	63.0	55.0	67.7
1943	54.2	57.1	59.3	69.0	77.7	82.2	82.1	83.4	75.1	66.0	55.9	53.0	67.9
1944	52.3	62.7	62.2	67.3	73.8	81.6	82.1	82.0	79.4	67.0	60.4	51.6	66.6
#1945	52.6	59.2	64.3	69.3	72.5	81.0	81.0	81.2	79.4	66.9	63.8	53.0	66.6
1946	51.4	55.2	62.2	69.4	74.4	79.6	81.0	81.4	78.0	70.3	63.0	56.2	66.7
#1947	57.4	47.6	55.0	69.6	73.6	81.2	81.4	83.2	79.8	74.3	57.6	53.7	67.5
1948	53.1	56.3	62.6	70.6	74.8	81.2	83.4	81.3	75.2	66.9	60.4	57.5	66.6
1949	57.3	59.3	60.4	65.3	75.4	80.3	81.9	80.4	76.1	72.6	57.8	56.4	66.4
1950	64.6	59.6	57.8	63.4	75.6	79.4	80.0	80.6	77.6	70.6	55.4	50.0	66.8
#1951	53.4	55.9	61.4	64.8	74.5	81.2	82.4	85.3	78.5	70.8	55.6	59.0	66.5
1952	63.1	58.9	59.1	64.4	74.8	82.4	82.4	82.9	76.4	62.3	56.9	52.7	67.7
1953	55.7	55.8	64.3	66.7	76.6	83.3	81.3	81.6	77.9	69.1	57.8	58.6	68.5
1954	54.5	59.3	59.8	71.9	70.7	81.5	82.6	83.1	79.7	69.8	57.7	52.9	68.6
1955	51.3	55.9	64.5	70.9	76.8	77.8	81.2	81.9	80.5	67.5	56.4	54.9	65.9
1956	58.6	59.0	60.3	66.9	76.9	78.0	82.9	81.7	77.1	70.1	57.6	60.3	68.9
1957	57.7	62.3	63.4	69.7	76.3	80.9	83.7	81.8	76.0	65.5	60.4	54.0	69.1
1958	47.3	47.3	57.3	68.6	75.6	81.5	82.7	81.0	79.6	66.3	61.6	50.5	66.8
#1959	48.5	55.3	59.9	67.3	76.6	80.0	82.0	82.1	77.6	71.6	54.9	53.5	67.7
1960	50.2	48.2	55.4	69.6	73.3	82.7	85.7	80.3	77.4	69.3	59.0	46.6	66.7
1961	44.3	54.9	63.4	62.7	71.7	76.4	78.8	78.1	76.9	66.9	57.9	53.9	65.4
1962	47.8	62.6	56.3	66.8	76.5	78.7	84.3	84.9	79.4	72.1	54.0	52.1	66.2
1963	47.1	49.0	65.1	72.4	76.0	81.0	82.3	82.3	79.0	72.1	59.0	45.3	67.7
1964	49.7	49.9	60.5	70.4	75.9	80.7	81.8	82.8	77.4	64.6	62.1	53.7	67.4
1965	53.2	53.1	56.0	71.9	75.2	79.1	81.6	79.6	76.1	66.1	64.3	53.5	67.8
1966	45.3	50.4	58.6	67.8	75.0	78.5	82.9	80.0	76.9	66.5	62.8	55.0	66.9
1967	51.5	50.7	64.7	72.8	72.9	80.3	79.9	80.3	74.5	65.2	56.9	54.4	67.2
1968	49.6	45.2	57.3	69.8	74.6	80.4	81.0	81.7	76.7	70.9	54.4	50.8	66.1
1969	53.9	53.9	53.8	68.6	74.6	81.0	83.5	80.9	77.3	70.3	57.6	52.4	67.3
1970	46.3	51.2	59.3	70.6	73.9	79.4	81.1	82.0	79.3	66.4	54.9	56.1	66.6
1971	52.6	53.2	57.2	66.4	72.7	80.8	81.9	81.7	78.7	72.6	57.9	62.7	68.2
1972	56.6	55.3	67.3	69.4	74.7	82.0	81.2	82.8	81.7	72.3	57.4	54.9	69.3
1973	49.3	51.3	65.3	65.1	74.1	81.4	84.4	80.4	79.9	73.3	64.2	52.9	66.7
1974	63.8	55.4	67.3	68.5	76.9	77.8	81.3	80.4	75.0	67.2	56.5	54.1	68.7
1975	55.3	57.2	60.5	66.5	73.9	79.6	81.4	81.0	74.7	67.8	59.7	51.8	67.6
1976	48.4	59.3	63.6	68.9	71.7	77.9	81.3	80.9	76.9	61.9	51.4	49.9	65.9
1977	41.6	53.3	62.3	67.9	75.4	82.5	83.3	81.3	79.7	66.4	61.9	52.7	67.4
1978	42.6	45.3	57.3	68.8	76.6	81.6	83.3	81.7	78.6	69.8	63.4	52.2	66.6
1979	42.9	50.3	60.5	68.9	72.5	79.3	81.5	80.9	76.0	68.8	54.9	50.0	65.9
1980	52.4	50.3	55.8	66.3	76.3	82.8	83.7	82.3	80.3	64.3	55.9	50.7	66.9
1981	46.3	52.6	59.3	72.6	71.9	81.7	83.4	82.4	76.3	68.4	62.2	51.4	67.4
RECORD MEAN	52.3	53.9	61.3	66.9	73.4	80.4	81.9	81.6	76.2	69.3	58.7	52.6	67.5
MAX	62.9	64.2	72.0	76.0	83.3	90.5	91.4	91.4	88.5	81.8	69.5	62.4	77.7
MIN	42.3	43.9	53.5	57.4	64.3	70.3	72.4	72.0	67.9	57.3	46.8	42.4	57.2

Heating Degree Days

Season	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	Total
1961-62	0	0	0	57	236	362	542	126	275	49	0	0	1669
1962-63	0	0	0	34	213	398	555	449	94	6	0	0	1753
1963-64	0	0	0	12	160	607	466	444	166	22	0	0	1897
1964-65	0	0	0	75	155	372	367	343	266	7	0	0	1605
1965-66	0	0	1	64	86	355	606	403	212	38	0	0	1765
1966-67	0	0	0	55	143	390	426	393	97	2	9	0	1515
1967-68	0	0	23	65	219	397	466	569	270	29	0	0	1975
1968-69	0	0	5	44	338	437	369	325	345	13	0	0	1865
1969-70	0	0	0	35	248	342	591	379	198	31	14	0	1870
1970-71	0	0	0	64	320	269	392	333	259	65	3	0	1736
1971-72	0	0	0	18	242	143	284	286	123	32	0	0	1122
1972-73	0	0	0	19	252	330	479	366	77	91	0	0	1648
1973-74	0	0	0	16	66	384	179	285	70	28	0	0	1050
1974-75	0	0	0	27	234	341	308	258	202	74	0	0	1458
1975-76	0	0	4	24	266	446	567	169	116	13	0	0	1547
1976-77	0	0	0	100	401	466	710	331	141	16	0	0	2205
1977-78	0	0	0	54	144	367	694	546	256	29	2	0	2116
1978-79	0	0	0	32	104	427	667	416	176	19	5	0	1870
1979-80	0	0	0	44	308	465	379	433	225	44	0	0	1898
1980-81	0	0	0	96	279	446	574	345	192	10	4	0	1952
1981-82	0	0	4	64	132	416							

Cooling Degree Days

Year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	Total
1969	20	10	2	133	305	484	579	501	375	207	26	0	2642
1970	14	2	22	211	261	436	507	531	435	111	6	20	2541
1971	21	12	28	137	249	481	530	523	421	236	35	77	2730
1972	38	15	44	163	307	519	507	550	506	250	46	33	2999
1973	0	2	92	117	292	446	407	499	455	202	128	15	2971
1974	53	21	142	141	300	590	511	465	329	103	49	33	2641
1975	30	34	64	124	329	444	515	500	302	154	94	16	2616
1976	2	23	87	123	195	394	506	501	367	51	2	0	2248
1977	0	4	77	111	337	535	573	513	447	121	42	12	2772
1978	0	0	18	129	371	522	567	526	424	131	63	32	2781
1979	0	0	44	141	233	430	521	501	336	144	34	6	2379
1980	0	15	40	64	352	514	586	539	461	75	15	10	2671
1981	0	3	17	227	224	509	561	553	350	176	56	4	2786

Precipitation

Year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	Annual
1942	5.56	4.13	5.05	10.18	3.76	10.54	4.08	10.66	5.40	4.44	0.47	6.95	71.05
1943	2.74	2.94	12.30	2.34	3.24	3.18	5.01	2.35	12.53	1.55	4.45	7.39	69.05
1944	6.72	2.60	4.95	4.29	4.22	4.92	2.46	9.93	3.46	1.04	7.60	3.74	56.35
#1945	7.54	6.07	4.16	6.37	3.52	4.84	5.22	6.30	5.93	4.21	2.70	4.73	61.93
1946	6.46	4.43	6.74	1.53	14.05	3.21	10.76	4.70	1.30	1.06	4.05	3.55	64.72
#1947	4.05	1.72	14.63	6.26	3.94	5.23	8.94	2.21	4.03	3.27	10.09	5.04	63.11
1948	5.13	3.53	6.41	3.34	3.64	1.71	2.67	4.78	5.43	1.23	12.98	5.76	56.96
1949	2.56	3.88	8.73	6.07	2.54	1.67	11.57	4.39	2.66	5.46	8.00	2.75	57.38
1950	7.21	4.29	6.54	6.55	3.32	8.92	5.41	8.96	8.57	1.35	1.43	6.49	53.24
#1951	5.50	1.11	6.00	2.23	1.07	2.32	7.44	1.42	4.56	0.38	2.77	4.07	39.69
1952	1.66	4.64	3.05	5.84	7.42	1.52	6.29	2.42	0.94	0.12	4.07	5.66	44.29
1953	2.99	6.72	5.17	6.63	10.70	2.71	5.45	6.04	0.01	0.45	5.07	13.23	65.98
1954	4.69	1.79	2.01	1.94	5.61	2.93	4.75	1.55	3.21	5.57	1.92	3.51	41.67
1955	4.44	5.52	8.54	8.35	4.20	3.53	6.19	3.63	3.57	2.20	4.81	3.31	58.49
1956	2.00	7.90	3.30	3.80	2.70	3.76	6.25	2.62	1.97	0.45	1.71	4.58	41.22
1957	1.88	4.17	5.96	6.08	2.67	4.56	7.30	3.60	6.48	3.24	6.27	3.14	55.35
1958	4.97	4.07	7.44	4.14	3.83	4.56	5.08	4.53	3.32	1.86	1.10	2.71	45.53
1959	4.72	8.51	2.23	3.26	8.91	4.19	10.11	5.38	3.21	3.04	1.31	3.67	61.54
1960	3.36	3.26	8.95	2.18	4.26	0.61	5.50	9.37	1.17	1.51	1.54	4.71	54.36
1961	5.20	11.33	5.44	4.63	3.40	3.67	10.94	2.54	9.47	0.66	7.43	8.19	73.92
1962	6.93	3.70	3.27	9.70	1.64	11.36	7.05	4.54	4.29	5.23	8.93	2.46	53.00
1963	3.64	3.67	0.61	0.81	0.63	4.11	10.98	3.46	1.90	0.23	4.32	5.19	41.91
1964	6.18	5.21	6.73	4.74	2.10	1.41	9.37	4.45	3.52	9.44	4.70	3.24	63.03
1965	2.63	5.93	4.50	1.43	3.90	1.83	4.50	7.83	5.20	0.93	2.40	4.71	45.00
1966	9.93	14.53	1.95	7.97	4.44	2.14	6.33	5.97	2.62	2.43	2.79	2.53	63.62
1967	2.39	4.03	1.90	12.64	7.73	2.76	4.32	4.11	3.46	2.17	8.25	5.95	57.84
1968	3.59	2.73	3.34	2.47	2.43	1.90	3.53	9.39	1.68	0.50	6.81	7.04	45.15
1969	1.34	5.44	5.42	10.23	2.92	0.76	9.83	3.79	2.99	6.84	0.52	3.79	53.06
1970	2.20	2.20	7.03	3.52	5.21	3.60	5.96	6.21	4.34	6.14	1.34	6.49	54.56
1971	1.19	4.39	5.27	0.75	3.71	2.37	9.59	5.13	18.94	2.63	3.17	10.04	59.06
1972	8.29	3.93	5.93	1.44	9.15	2.43	6.34	1.98	4.12	3.64	4.75	8.22	59.77
1973	4.08	3.64	12.73	10.17	5.40	2.99	4.36	4.93	13.08	1.09	7.44	6.29	79.03
1974	8.33	6.44	5.64	5.59	5.23	1.11	5.89	6.45	2.19	1.63	4.55	3.70	56.97
1975	7.77	1.43	4.49	10.18	5.44	5.11	9.30	11.69	3.54	2.58	2.16	2.37	66.10
1976	3.72	4.67	5.18	0.38	4.92	4.90	7.65	2.31	1.96	3.18	5.00	5.80	49.07
1977	6.50	3.69	4.65	7.10	3.97	1.46	6.35	11.31	13.93	3.89	10.35	2.97	77.78
1978	6.59	2.24	1.64	2.92	7.43	2.94	7.19	7.54	3.03	T	4.94	1.94	49.33
1979	6.29	10.83	4.26	11.47	5.37	0.17	8.76	4.94	3.55	2.43	5.06	2.82	65.91
1980	4.63	3.56	6.25	14.64	7.26	5.35	7.48	1.32	7.74	5.64	5.57	2.38	74.30
1981	1.20	7.07	1.74	3.09	4.47	4.70	4.25	4.46	3.95	1.62	1.51	5.35	43.21
RECORD MEAN	4.93	4.68	5.04	4.90	4.90	4.27	6.58	5.40	4.28	2.93	3.86	5.12	56.88

Snowfall

Season	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	Total
1970-71	0.0	0.0	0.0	0.0	0.0	0.0	0.0	T	0.0	0.0	0.0	0.0	T
1971-72	0.0	0.0	0.0	0.0	0.0	0.0	T	0.0	0.0	0.0	0.0	0.0	T
1972-73	0.0	0.0	0.0	0.0	0.0	0.0	0.6	1.8	0.0	0.0	0.0	0.0	2.4
1973-74	0.0	0.0	0.0	0.0	0.0	T	0.0	0.0	0.0	0.0	0.0	0.0	T
1974-75	0.0	0.0	0.0	0.0	0.0	0.0	T	0.0	0.0	0.0	0.0	0.0	T
1975-76	0.0	0.0	0.0	0.0	0.0	0.0	T	0.0	0.0	0.0	0.0	0.0	T
1976-77	0.0	0.0	0.0	0.0	T	0.0	T	0.0	0.0	0.0	0.0	0.0	T
1977-78	0.0	0.0	0.0	0.0	0.0	0.0	T	0.0	0.0	0.0	0.0	0.0	T
1978-79	0.0	0.0	0.0	0.0	0.0	0.0	T	0.0	0.0	0.0	0.0	0.0	T
1979-80	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	T	0.0	0.0	0.0	T
1980-81	0.0	0.0	0.0	0.0	0.0	0.0	T	T	0.0	0.0	0.0	0.0	T
1981-82	0.0	0.0	0.0	0.0	0.0	0.0							
RECORD MEAN	0.0	0.0	0.0	0.0	T	T	T	0.2	T	0.0	0.0	0.0	0.2

# Indicates a station move or relocation of instruments. See Station Location table.

Record mean values above are means through the current year for the period beginning in 1893 for temperature and precipitation, 1951 for snowfall. Data are from cooperative locations through April 1943.

STATION LOCATION

BATON ROUGE, LOUISIANA

Location	Occupied from	Occupied to	Airline distance and direction from previous location	Latitude North	Longitude West	Elevation above Sea level: Ground at temperature site	Elevation above Ground: Wind instruments	Extreme thermometers	Psychrometer	Sunshine Switch	Tipping bucket rain gage	Weighing rain gage	8" rain gage	Hygrothermometer	Automatic Observing Equipment *	* Type S = AMOS T = AUTOB	Remarks
COOPERATIVE																	
Old LSU campus (now State Capitol grounds)	2/1888	9/1908	NA	30° 27'	91° 11'	55		6					3				
Bluff overlooking river; South end of business District	10/1908	5/1922	0.8 mi. SSE	30° 27'	91° 11'	60		6					8				
Statehouse grounds; 3rd Street & North Blvd.	6/1922	1933	1 block NE	30° 27'	91° 11'	60		6					11				Thermometers at Statehouse; rain gage at observers' homes.
Richland & Government Streets	1933	6/1946	3.5 mi. E	30° 27'	91° 09'	56		6					3				Moved by observer for his convenience in observing.
AIRPORT																	
Administration Building Municipal Airport	6/4/32	9/14/41	NA	30° 27'	91° 07'	56	60		4								Operated on scheduled flight basis to 9/15/41. Operated jointly by CAA and Army Air Force 9/15/41-5/11/42.
Harding Field	4/12/42	2/25/45	8 miles N	30° 32'	91° 09'	64											USAF station established 5/12/42.
Harding Field Building 173	2/25/45	5/26/45	Unknown	30° 32'	91° 09'	68	25	4	4				3				USAF station closed and Weather Bureau office opened.
Harding Field Building 103	5/26/45	1/12/48	0.75 mi. E	30° 32'	91° 09'	64	28	6	6				3				
Harding Field, Hanger	1/12/48	5/15/51	800 ft. S	30° 32'	91° 09'	64	69	55	55			46	46				
Terminal Building Harding Field †	5/15/51	10/20/78	1000 ft. N	30° 32'	91° 09'	64	70 a20	19 f	19	NA	NA d4 g18	18 c4 g18	18 c4 g18	NA b4 e5	NA		a - Moved 1300' ESE 2/15/59. b - Commissioned 1300' ESE of thermometer site 8/4/59. c - Effective 2/10/67. d - Installed 2/25/67. e - Effective 4/67. f - Removed 1/7/70. g - Moved to roof 8/4/73.
† Ryan Airport (Effective 3/10/54)																	
Nat. Wea. Service Bldg. Airport	10/20/78	Present	3960 ft.ESE	30° 32'	91° 08'	64	h20	NA	5	NA	4	4	4	5	NA		h - Not moved 10/20/78.

SUBSCRIPTION: Price and ordering information available through: National Climatic Center, Federal Building, Asheville, N. C. 28801, ATTN: Publications.

I certify that this is an official publication of the National Oceanic and Atmospheric Administration, and is compiled from records on file at the National Climatic Center, Asheville, North Carolina 28801.

Director, National Climatic Center

USCOMM-NOAA-ASHEVILLE - 1100

BATON ROUGE WIND ROSE

ANNUAL (1965-1974)

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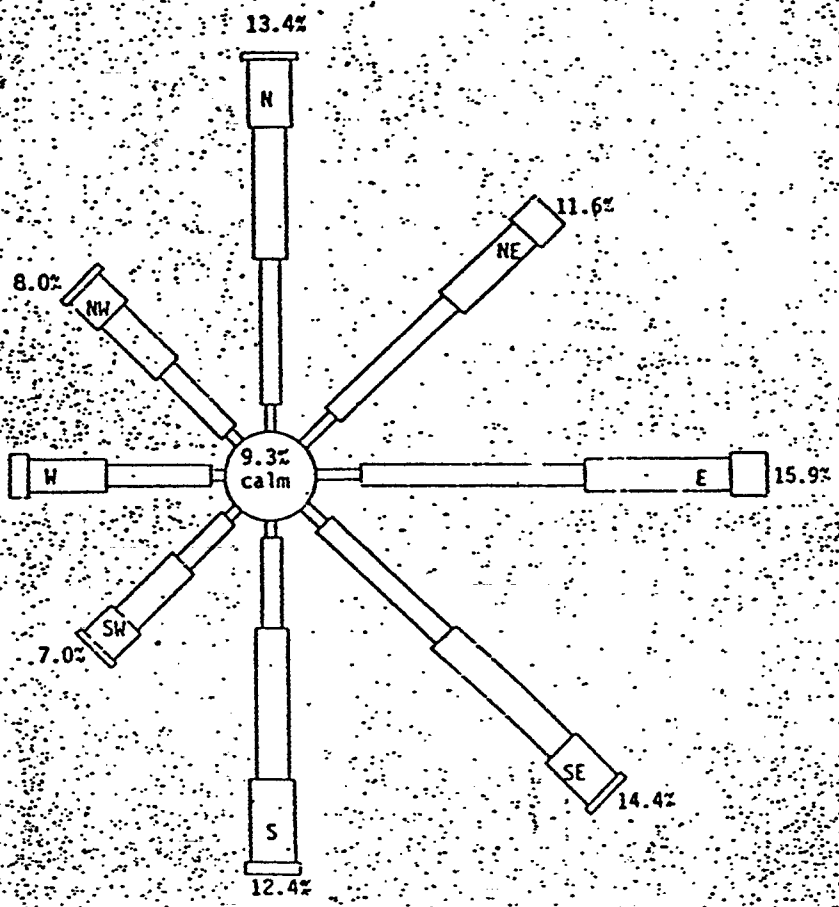
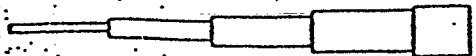
BY THE LOUISIANA OFFICE OF STATE CLIMATOLOGY AT LOUISIANA STATE UNIVERSITY

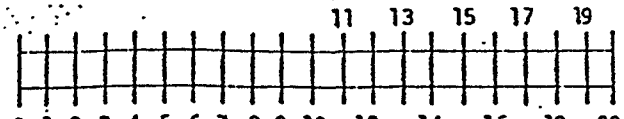


Speed Classes (mph)



direction from which the wind is blowing

1-3 4-7 8-12 13-18 19+



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BATON ROUGE WIND ROSE

SPRING (MARCH, APRIL, MAY)(1965-1974)

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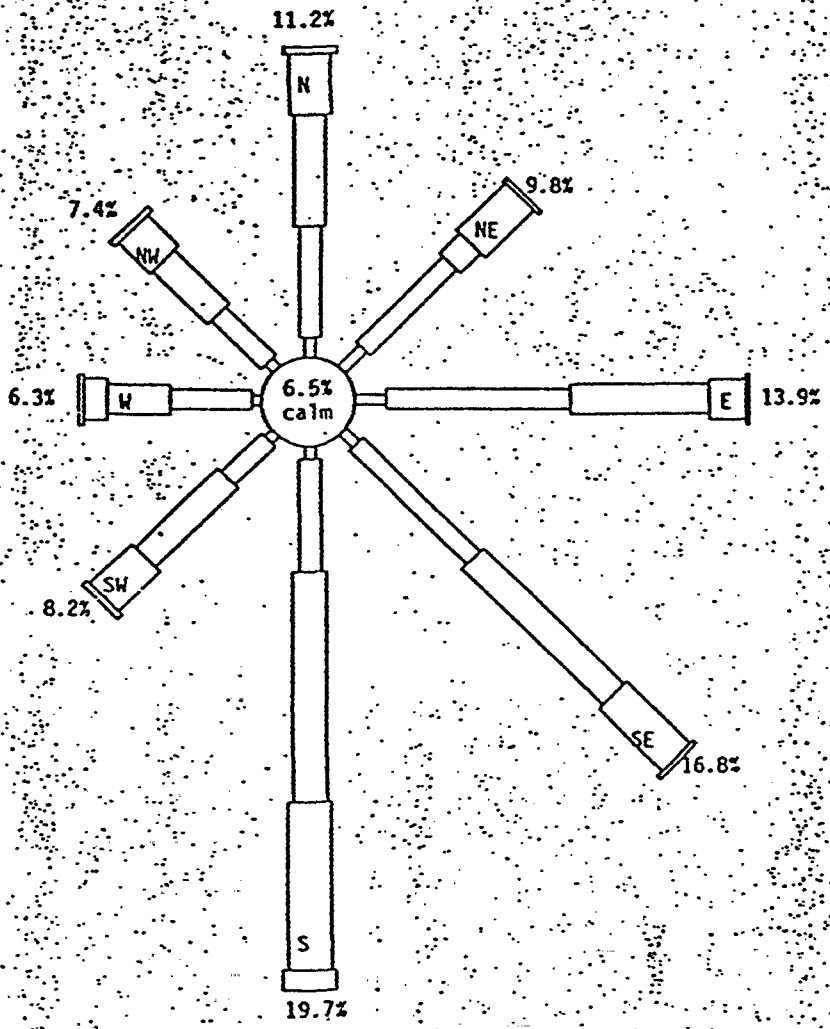
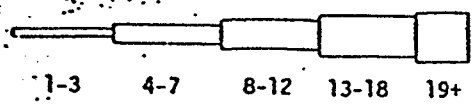
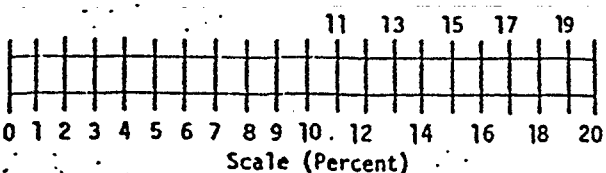


Speed Classes (mph)



direction from which the wind is blowing

1-3 4-7 8-12 13-18 19+



Scale (Percent)

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BATON ROUGE WIND ROSE

SUMMER (JUNE, JULY, AUGUST)(1965-1974)

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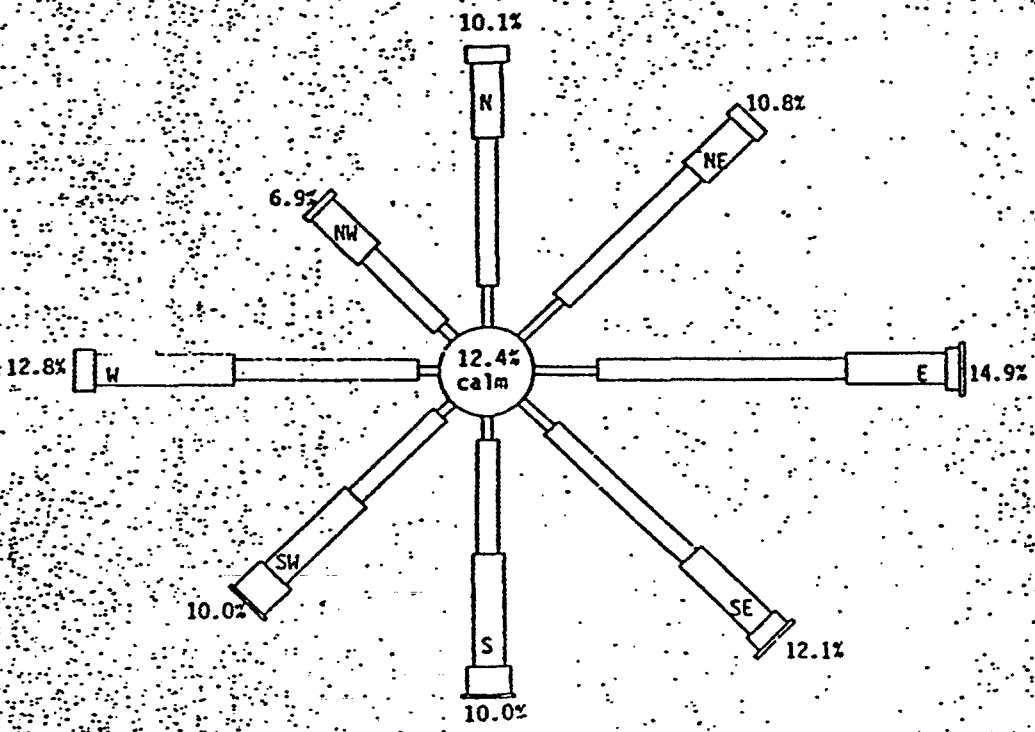

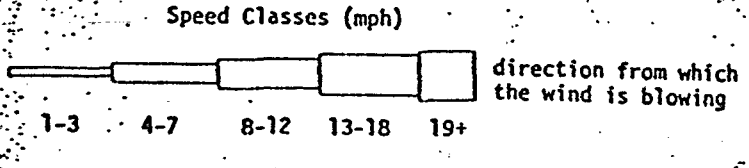

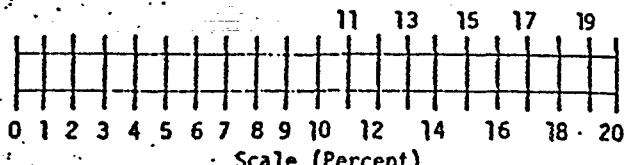

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BATON ROUGE WIND ROSE

FALL (SEPTEMBER, OCTOBER, NOVEMBER)(1965-1974)

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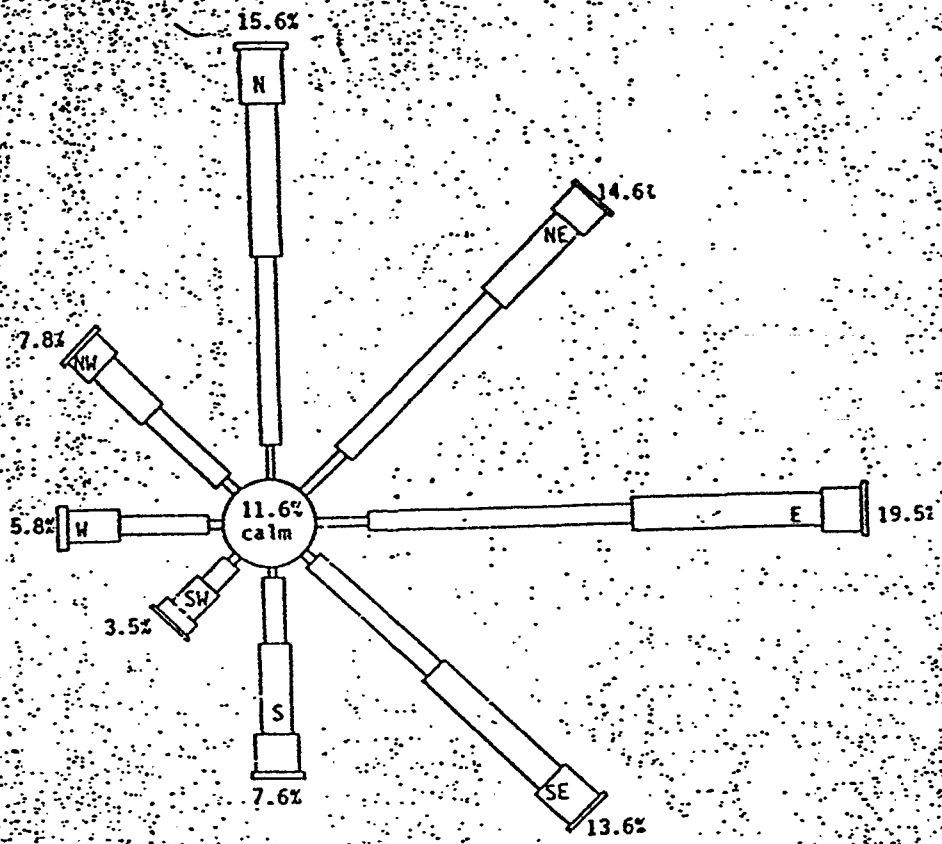

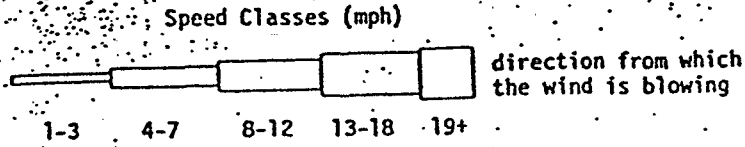

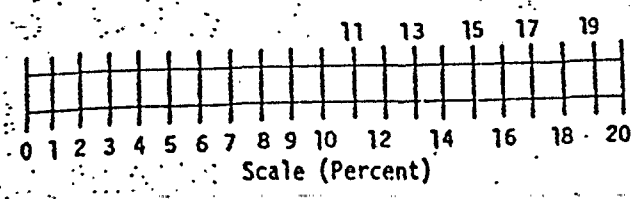

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BATON ROUGE WIND ROSE

WINTER (DECEMBER, JANUARY, FEBRUARY)(1965-1974)

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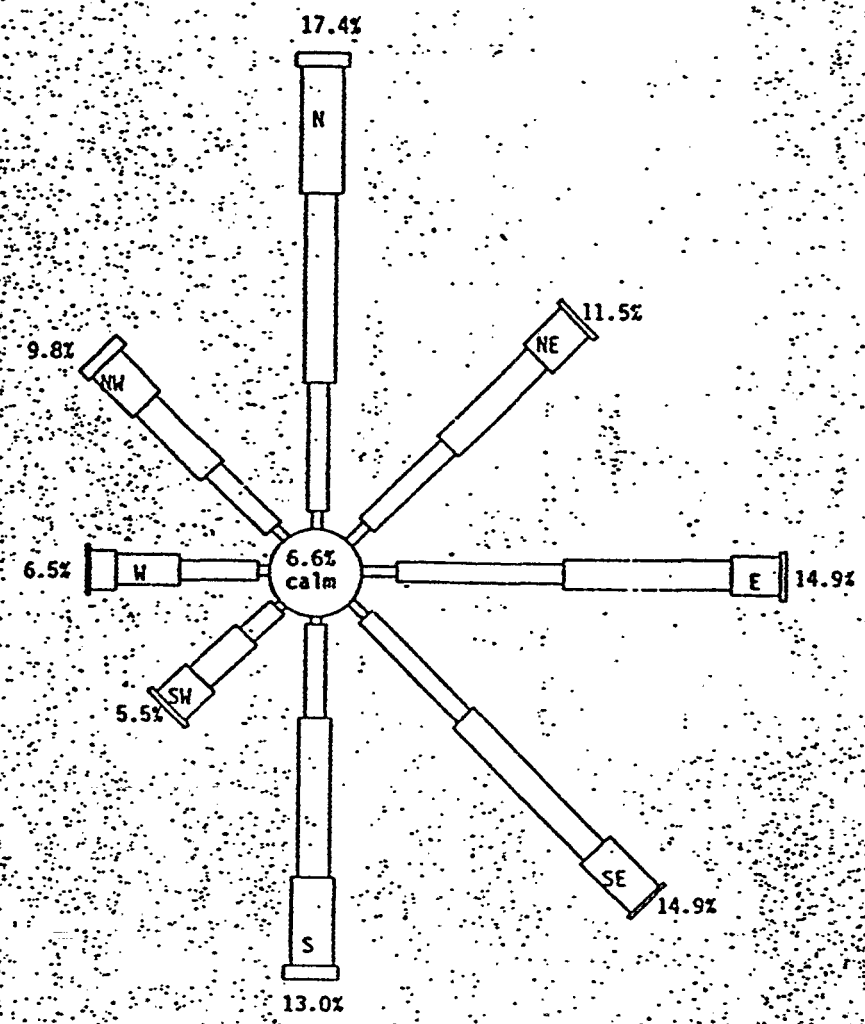

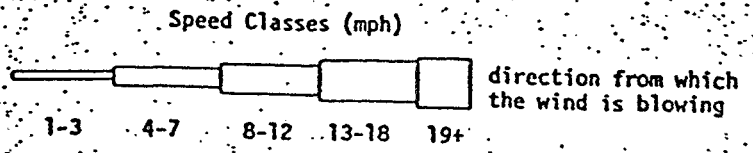

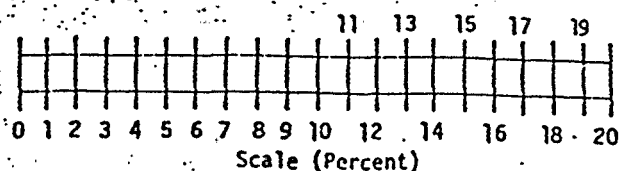

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