

FINAL REPORT

TOXIC POINT SOURCE ASSESSMENT OF INDUSTRIAL DISCHARGES TO THE CHESAPEAKE BAY BASIN. PHASE III: PROTOCOL VERIFICATION STUDY

**VOLUME II
APPENDICES B - C**

Contract 68-02-3161

August 1982

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY



**D A Y T O N
L A B O R A T O R Y**

DAYTON, OHIO 45407

903R81105

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CHESAPEAKE BAY BASIN. PHASE III: PROTOCOL VERIFICATION STUDY

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APPENDICES B-C

by

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Dayton, Ohio 45418

Contract 68-02-3161

August 1982

Project Officer

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Annapolis, Maryland 21401

CHESAPEAKE BAY PROGRAM OFFICE
TOXICS PROGRAM
U.S. ENVIRONMENTAL PROTECTION AGENCY
ANNAPOLIS, MARYLAND 21401

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APPENDIX B
PHASE III PLANT PRESURVEY REPORTS

The reader is referred to Section 3 for a discussion of how the plant presurveys were conducted.

These presurvey reports are designed to use as a guide for gathering useful information about an industrial site before it is actually sampled. Presurvey sheets can be tailored to the needs of the researchers conducting the study; the important point to be made is the necessity of "upfront planning." Careful planning before the sampling date can help minimize poor or incomplete data gathering and the resulting need for resampling a site.

PRESURVEY DATA SHEETS

I. NAME OF COMPANY #A 109 DATE OF SUMMARY _____

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL D.W. Down PHONE 513-268-3411

S.C. Wilson PHONE 513-268-3411

EPA PERSONNEL _____ PHONE _____

_____ PHONE _____

STATE PERSONNEL _____ PHONE _____

_____ PHONE _____

INDUSTRY TYPE Chemical Manufacturing

PORTION OF PROCESS TO BE SAMPLED outfall 001, major process
outfall and blowdown from wet scrubber

II. PROCESS DESCRIPTION Plant is engaged in the manufacture
of Industrial inorganic chemicals & amines, see att.

II. Con't.

Raw materials and amounts SEE IPPEU

Fuels #6 Oil

Products and amounts SEE N.P.D.E.S.

Operating Cycle:

Check: Batch ✓ Continuous ✓ Cyclic ✓

Timing of batch or cycle —

Best time to sample Anytime

Length of Operating day 24 hrs

Length of operating week 7 days

Scheduled shutdowns None

Other —

III. WASTEWATER TREATMENT PLANT DESCRIPTION: SEE ATTACHED Figures

Chemicals added and amounts lime, H_2SO_4

Handles rainfall runoff? Some

Includes sanitary waste, flow No

Source of plant intake water Mostly RIVER

Hydraulic retention time: Thru plant —
Thru treatment unit operations 40 days

Recent treatment plant performance Normal-good

III. Con't.

NPDES permit parameters and limits BOD (), SS (),
Zn (), NH₃ (), Sulfides (), pH ()

Final effluent flow rate 1-1.1 MGD

List of potential pollutants SEE ATTACHMENT

Recent analyses available? SEE DMR's

Sampling point description AT BRIDGE NEAR METAL BUILDINGS

Use automatic sampler? yes

Electricity available yes

Extension cord and type of outlet? 25 FT, 110V, 3 prong

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

<u>Item</u>	<u>Plant</u>	<u>MRC</u>	<u>Item</u>	<u>Plant</u>	<u>MRC</u>
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions NO
2. Vehicle traffic rules NONE in PARTICULAR
3. Possible set-up/clean-up facilities? SEE PLANT CONTACT
4. Evacuation procedures NONE
5. Alarms NONE
6. Hospital location —
7. Hospital Phone SEE PHONE BOOK
- Emergency Numbers —

V. Plant Entry

- A. Plant Requirements SEE PLANT CONTACT
- Special time constraints: SEE PLANT CONTACT
- B. MRC Agreement CONFIDENTIALITY
- C. Potential Problems NONE

VI. SAMPLING HANDLING

A. Ice availability SEE PLANT CONTACT

B. Sample splitting requested yes

Describe SEE PLANT CONTACT

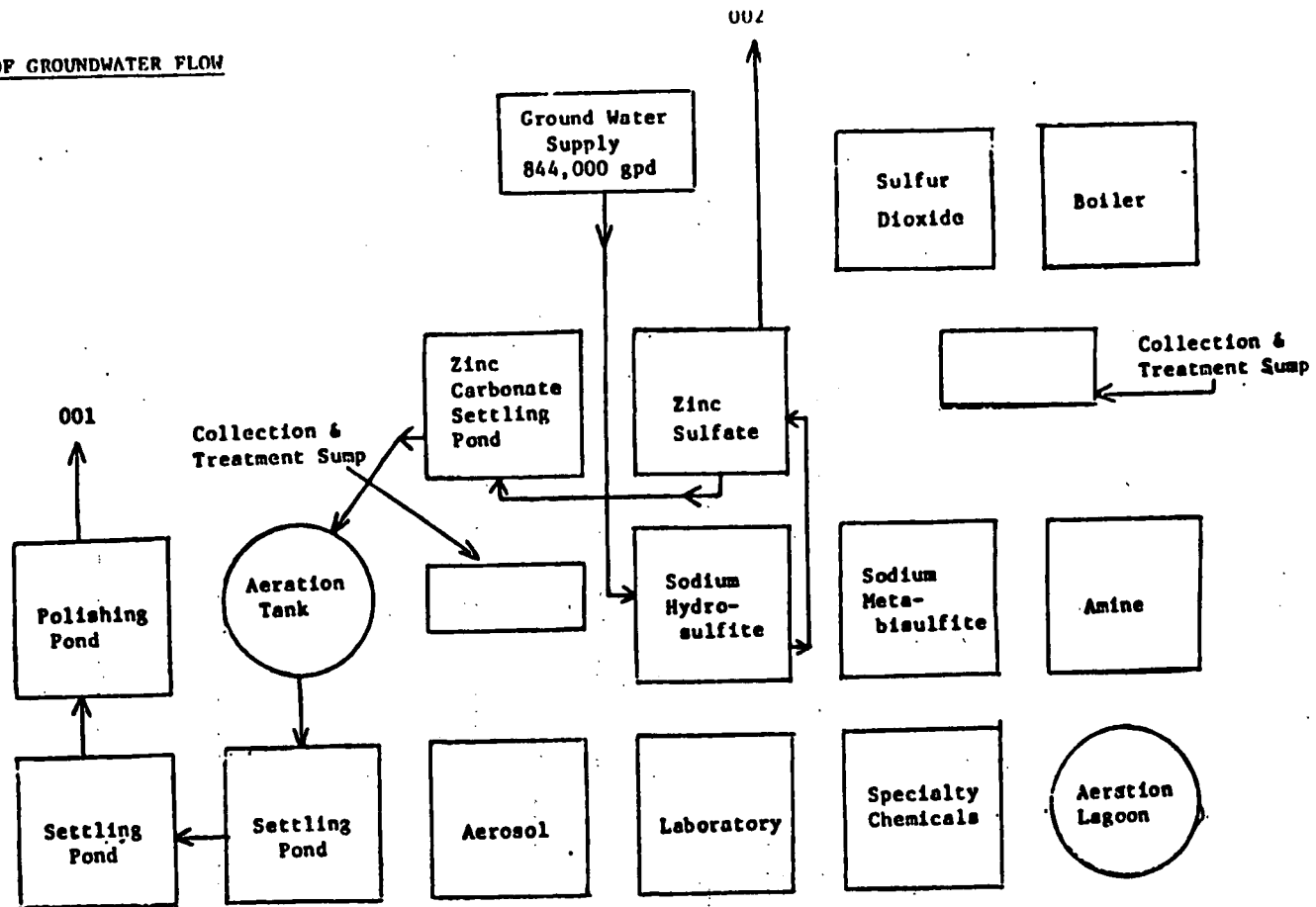
C. Nearest airport: _____

D. Chemical available: ~~H₂SO₄~~ _____

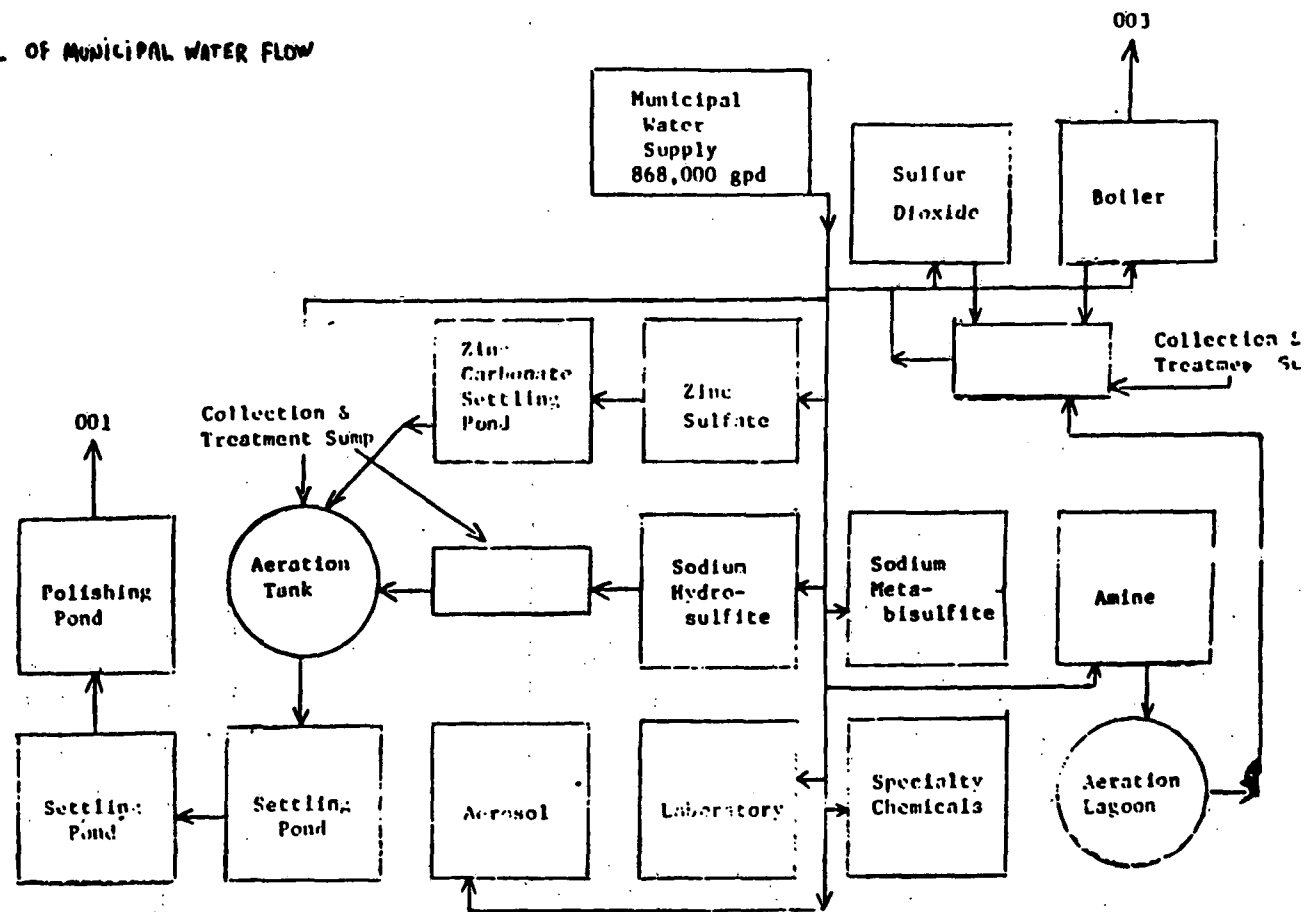
~~HNO₃~~ _____

~~NaOH~~ _____

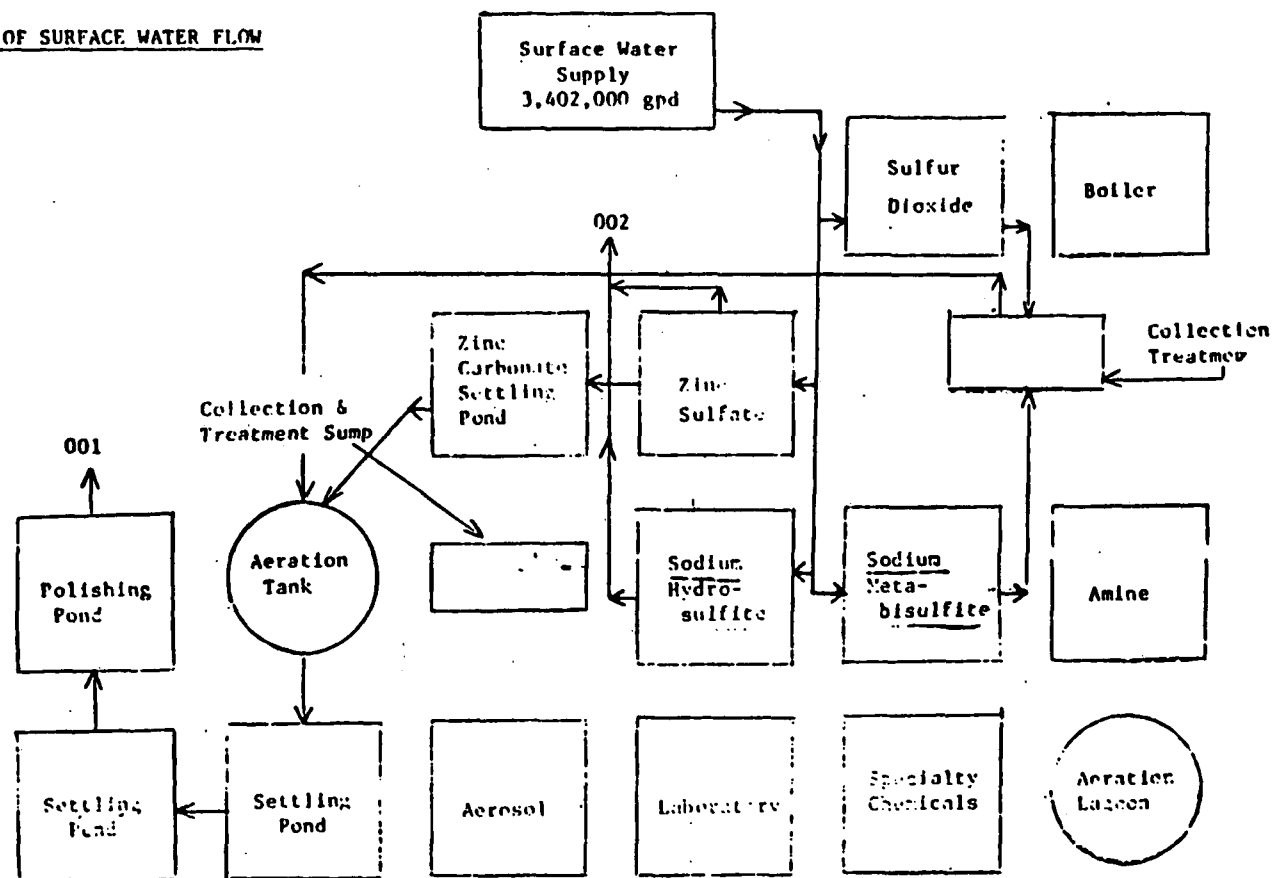
SCHEMATIC OF GROUNDWATER FLOW



B-8



SCHEMATIC OF SURFACE WATER FLOW



#A 109

Compounds to be specifically
semi quantified
(Amines)

propyl

butyl

isobutyl

ethyl

isopropyl

octyl

2-ethylhexyl

cyclohexyl

PRESURVEY DATA SHEETS

I. NAME OF COMPANY B/I/D DATE OF SUMMARY _____

ADDRESS _____ PHONE _____

NAME OF CONTACTS information available

MRC PERSONNEL David Dunn PHONE (513) 268-3411

David Vanek PHONE _____

EPA PERSONNEL _____ PHONE _____

STATE PERSONNEL _____ PHONE _____

INDUSTRY TYPE Wood Preservatives (SIC 2491)

PORTION OF PROCESS TO BE SAMPLED Sample storm sewer At last Manhole (See diagram)

II. PROCESS DESCRIPTION Wood treating and preserving via batch processes using pentachlorophenol and creosote. Treats piling, poles, ties and sawed lumber.

II. Con't.

piling - 800 K ft³
poles - 800 K ft³
lumber - 100 K ft³
ties - 400 K ft³
Switch ties - 25 K ft³
Raw materials and amounts 1 x 10⁶ gal creosote/yr.
600 K gal pentachlorophenol
Fuels #6 fuel oil and wood waste - 40:60%
Products and amounts Piling 700 K ft³
poles 700 K ft³
Operating Cycle: lumber 100 K ft³
Crossties 25 K ft³
Check: Batch X Continuous _____ Cyclic _____
Timing of batch or cycle 15-22 hrs
Best time to sample during rain fall or soon after
Length of Operating day 24 hrs. (treating room only)
Length of operating week 5 days
Scheduled shutdowns holidays
Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: Run waste water in liquid
incinerator - only waste water discharge is from storm runoff.

Chemicals added and amounts _____
Handles rainfall runoff? yes
Includes sanitary waste, flow No
Source of plant intake water Municipal
Hydraulic retention time: Thru plant _____
Thru treatment unit operations No wastewater treatment due to
incineration of wastewater.
Recent treatment plant performance _____

III. Con't.

NPDES permit parameters and limits Oil and grease (10 mg/l),
Phenolics (1 mg/l), TSS (20 mg/l)

Final effluent flow rate N/A

List of potential pollutants see attachment

Recent analyses available? No

Sampling point description storm sewer bordering plant site.
Handles rainwater runoff of roadway, small section of plant site including
creosote saturated area, and some runoff from other plant sites in area.

Use automatic sampler? yes

Electricity available None

Extension cord and type of outlet? None

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

<u>Item</u>	<u>Plant</u>	<u>MRC</u>	<u>Item</u>	<u>Plant</u>	<u>MRC</u>
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
Boots		✓	First aid		✓

B. SAMPLE SITE

1. Smoking restrictions None
2. Vehicle traffic rules None
3. Possible set-up/clean-up facilities? Foremen's room
4. Evacuation procedures Stay at sample site
5. Alarms Whistle at 8:00am
6. Hospital location Information available
7. Hospital Phone Information available
- Emergency Numbers _____

V. Plant Entry

- A. Plant Requirements Register at office - alert for night visit.

Special time constraints: _____

- B. MRC Agreement _____

- C. Potential Problems _____

VI. SAMPLING HANDLING

A. Ice availability See Lab Technician

B. Sample splitting requested yes

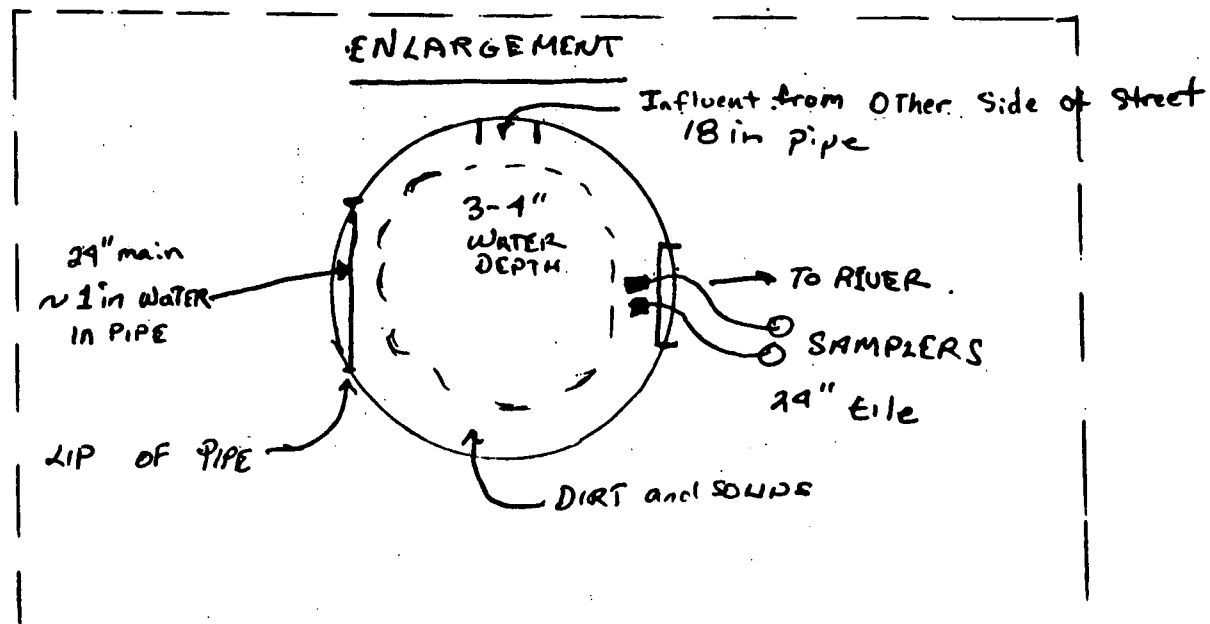
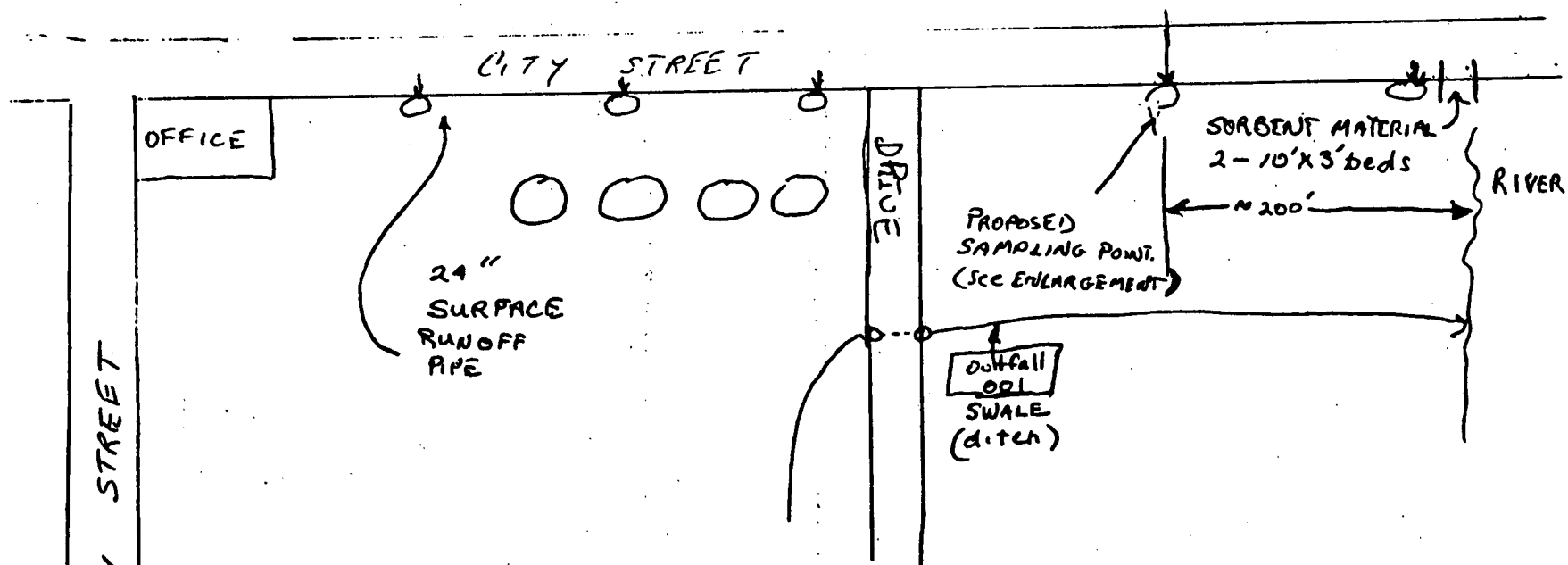
Describe 1 gal to check ^{perm} parameters

C. Nearest airport: _____

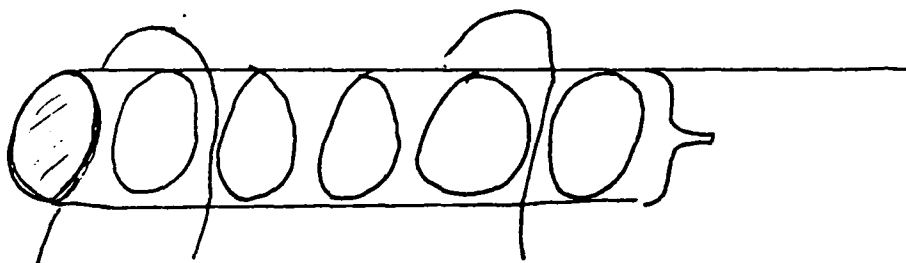
D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____



SAMPLING PROBE MODIFICATIONS



←
CLOSE HANGER FEET
TO PROBE ≈ 1 in
OFF BOTTOM

Justification for Toxic compound selection

An analysis of each production process was undertaken to evaluate those pollutants which could potentially be present in the process effluent. Emphasis was placed on pollutants potentially present due to production and/or subsequent wastewater treatment.

This analysis typically involved first a compilation of information from respective NPDES permit files. This information, yielding location, type or types of processes, general flow diagrams, etc., was then applied to the list of references for each presurvey report. These additional references yielded information regarding reactants, products, byproducts, general unit operations employed and their parameters, plant specific information where known, experience with similar plants or industries, and finally, actual wastewater characterization data for each industry type.

Possible pollutant sources in the process wastewaters included water as a product of combustion or other process reaction, direct contact cooling water, product wash water, reactor washout wastes, condenser and scrubber water which has contacted either products or reactants, non-contact cooling water which may be contaminated due to process flange leaks, etc and finally, pollutants which may be produced as a result of the wastewater treatment system unit operations.

The analysis protocol for Phase I calls for automatic monitoring NPDES parameters, phenol, cyanide, inorganic ions and 76 elemental compounds. Therefore, organic compounds are the major output of this exercise.

No formal consideration was given to possible background contamination; e.g. plant intake waters, as the program is concerned with the contribution emanating from a particular production point source.

The list of organic compounds finally generated was evaluated to determine the toxicity of its members.

As stated in the project work plan, those compounds suspected to be particularly toxic are to be semi-quantified, whenever possible, with the remainder of the list scanned for via mass spectrometry.

The toxicity evaluation parameters were as follows:

Any lethality rating $< 500 \text{ mg/kg}$	→ semi-quantify
Any identified carcinogenicity	→ semi-quantify
Any identified mutagenicity	→ semi-quantify
Any identified teratogenicity	→ semi-quantify
Any known toxic decomposition products	→ semi-quantify
None of the above	→ qualify via M. S.

Plant B1120 has no direct process discharge. A groundwater seepage from creosote laced soil to city storm drainage is of concern here. The constituents of creosote and other related wood treating compounds are expected to be found here.

Suspected Pollutants

Phenol *

Benzene *

Ethyl benzene

Toluene *

Acenaphthalene *

Pentachlorophenol *

2,4-Dimethylphenol

2,4-Dichlorophenol *

Fluorene *

Diphenylene oxide *

Carbazole *

2-Chlorophenol *

2,4,6-Trichlorophenol *

* To be semi-quantified due to potential toxicity, carcinogenicity, mutagenicity or teratogenicity

All sampling and testing methods for this plant are anticipated to be identical to those outlined in the project work plan, dated 26 November, 1979. Any deviations are noted herein.

References

1. Gerstle, R., and J. Richards. Industrial Process Profiles for Environmental Use. EPA-600/2-77-023d, U.S. Environmental Protection Agency, Cincinnati, OHIO, February 1977.
2. Letkiewicz F. Chemicals Which Have Been Tested for Neurotoxic Effects. EPA-360/1-76-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1976. 1332 pp.
3. Markle, R. A., Fentiman, A. F., Steadman, T. R. and R. A. Mayer. An Assessment of the Treatment and Control of Wastes From the Manufacture and Use of Potentially Toxic and Hazardous Organic Chemicals. U.S. Environmental Protection Agency (Patelle Columbus Laboratories Contract Number 68-02-1323). Cincinnati, OHIO, June 1974. 290 pp.

4. Watkins, DR. Review of Industrial Organic Chemicals Processes for Potentially Toxic Materials. Contract Number 68-03-2579. Environmental Protection Agency, Cincinnati, Ohio, August, 1978.
5. STANDARD INDUSTRIAL CLASSIFICATION MANUAL, Executive Office of the President / BUREAU OF THE BUDGET, 1976. pp 615.
6. Dorigan, J., Fuller, B. and R. Duffy. Scoring of Organic Air Pollutants Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals. Contract Number 68-02-1495, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1976. 331 pp.
7. Fairchild, E. J. Registry of Toxic Effects of Chemical Substances. Contract Number 210-75-0034, U.S. Department of Health, Education and Welfare. 1977 edition.
8. U.S. EPA Wastewater Treatability Manual, draft Monsanto Research Corp. 1979.
9. State and Region NPDES permit files.

PRESURVEY DATA SHEETS

I. NAME OF COMPANY B119D DATE OF SUMMARY _____
ADDRESS _____ PHONE _____

NAME OF CONTACTS Information available

MRC PERSONNEL David Dunn PHONE 513(268-3411)
David Vanek PHONE _____
EPA PERSONNEL _____ PHONE _____

PHONE _____
STATE PERSONNEL _____ PHONE _____

PHONE _____
INDUSTRY TYPE Polyester Film (SIC 3079)

PORTION OF PROCESS TO BE SAMPLED OOI Outfall

II. PROCESS DESCRIPTION Establishment primarily engaged in molding
primary plastics for trade and fabricating miscellaneous
finished plastic products. Produces polyester film as
primary product. _____

II. Con't.

Raw materials and amounts Ethylene glycol
Dimethyl terephthalate (DMT)
Fuels No 2 fuel oil,
Products and amounts Polyester film

Operating Cycle:

Check: Batch X Continuous X Cyclic

Timing of batch or cycle Several batch operations running Continuous

Best time to sample Week day

Length of Operating day 24 hrs

Length of operating week 7 day

Scheduled shutdowns No

Other Bio system: Scheduled sampling may not give good representative analysis results because the bio system will not have had time to equilibrate. It is suggested that June would be better period for sampling.

III. WASTEWATER TREATMENT PLANT DESCRIPTION: activated sludge (aerobic) for sanitary waste only.

blowdown is combined with sanitary waste treatment

Pretreatment is for the control of corrosion and biocides

Bio activated sludge facility to be built by the first of April

Note - No actual waste water treatment - treat with muriatic

acid for pH control

Presently No actual wastewater treatment practices other than incineration of wastewater.

Chemicals added and amounts Muriatic acid

Handles rainfall runoff? yes

Includes sanitary waste, flow yes (15,000 gpd)

Source of plant intake water Well water

Hydraulic retention time: Thru plant

Thru treatment unit operations N/A at this time

Recent treatment plant performance

III. Con't.

NPDES permit parameters and limits* BOD₅ ((500 lb/day) (893 lb/day))
TSS (340 lb/day) (610 lb/day) PH (6.0-8.5)

Final effluent flow rate 50,000 gpd (most is runoff) flow may vary

List of potential pollutants considerably see attachment

Recent analyses available? No

Sampling point description Outfall 001, Combined waste from sanitary, blowdown, surface water

Use automatic sampler? yes

Electricity available 110 V

Extension cord and type of outlet? 25 ft, three prong

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

<u>Item</u>	<u>Plant</u>	<u>MRC</u>	<u>Item</u>	<u>Plant</u>	<u>MRC</u>
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

* These limits will change with introduction of New Biosystem
 As Soon as EPA approves. B-26

B. SAMPLE SITE

1. Smoking restrictions Smoking prohibited
2. Vehicle traffic rules Minimum traffic & truck checked in at yard house, speed limit 15 mph
3. Possible set-up/clean-up facilities? Yes
4. Evacuation procedures Stay in area
5. Alarms Intercom system
6. Hospital location Information available
7. Hospital Phone Information available
- Emergency Numbers First Aid Team on site

V. Plant Entry

- A. Plant Requirements pass issued - none for vehicle - will be accompanied continuously

Special time constraints: None

- B. MRC Agreement

- C. Potential Problems

VI. SAMPLING HANDLING

A. Ice availability See Area STORE

B. Sample splitting requested yes

Describe Organics (2-3 gal) and inorganics

C. Nearest airport: Information Available

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

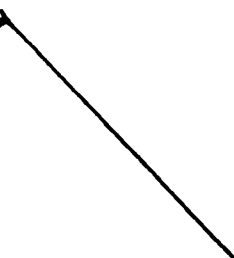
PLANT B1190 WASTE TREATMENT
POLYESTER FILM PRODUCTION

CONCENTRATED
WASTEWATER

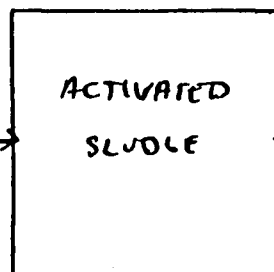


INCINERATED
BY VENDOR

BLUDDOWN
COOLING WATER,
STEAM AND
SURFACE WATER



SANITARY
WASTE



CHLORINE



MURIATIC ACID



DISCHARGE

* Sample Collection Point

Justification for Toxic compound selection

An analysis of each production process was undertaken to evaluate those pollutants which could potentially be present in the process effluent. Emphasis was placed on pollutants potentially present due to production and/or subsequent wastewater treatment.

This analysis typically involved first a compilation of information from respective NPDES permit files. This information, yielding location, type or types of processes, general flow diagrams, etc., was then applied to the list of references for each presurvey report. These additional references yielded information regarding reactants, products, byproducts, general unit operations employed and their parameters, plant specific information where known, experience with similar plants or industries, and finally, actual wastewater characterization data for each industry type.

Possible pollutant sources in the process wastewaters included water as a product of combustion or other process reaction, direct contact cooling water, product wash water, reactor washout wastes, condenser and scrubber water which has contacted either products or reactants, non-contact cooling water which may be contaminated due to process flange leaks, etc and finally, pollutants which may be produced as a result of the wastewater treatment system unit operations.

The analysis protocol for Phase I calls for automatic monitoring NPDES parameters, phenol, cyanide, inorganic ions and 76 elemental compounds. Therefore, organic compounds are the major output of this exercise.

No formal consideration was given to possible background contamination; e.g. plant intake waters, as the program is concerned with the contribution emanating from a particular production point source.

The list of organic compounds finally generated was evaluated to determine the toxicity of its members.

As stated in the project work plan, those compounds suspected to be particularly toxic are to be semi-quantified, whenever possible, with the remainder of the list scanned for via mass spectrometry.

The toxicity evaluation parameters were as follows:

Any lethality rating $< 500 \text{ mg/kg}$	→	semi-quantify
Any identified carcinogenicity	→	semi-quantify
Any identified mutagenicity	→	semi-quantify
Any identified teratogenicity	→	semi-quantify
Any known toxic decomposition products	→	semi-quantify
None of the above	→	qualify via M. S.

Plant B119D is engaged in the manufacture of various glycols. Compounds selected are directly used in the process or are potential by-products which could end up in the discharge streams.

Suspected Pollutants

Ethylene glycol *
Ethylene oxide *
Acetaldehyde *
Crotonaldehyde *
Diethylene glycol
Triethylene glycol
Polyethylene glycol
Methanol *
Propylene glycol *
Phthalic anhydride *
Maleic anhydride *

* To be semi-quantified due to potential toxicity, carcinogenicity, mutagenicity or teratogenicity

All sampling and testing methods for this plant are anticipated to be identical to those outlined in the project work plan, dated 26 November, 1979. Any deviations are noted herein.

References

1. Gerstle, R., and J. Richards. Industrial Process Profiles For Environmental Use. EPA-600/2-77-023d, U.S. Environmental Protection Agency, Cincinnati, OHIO, February 1977
2. Letkiewicz F. Chemicals Which Have Been Tested for Neurotoxic Effects. EPA-360/1-76-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1976. 1332 pp.
3. Markle, R.A., Fentiman, A.F., Steadman, T.R. and R.A. Mayer. An Assessment of the Treatment and Control of Wastes From the Manufacture and Use of Potentially Toxic and Hazardous Organic Chemicals. U.S. Environmental Protection Agency (Patelle Columbus Laboratories Contract Number 68-02-1323). Cincinnati, OHIO, June 1974. 290 pp.

4. Watkins, D.R. Review of Industrial Organic Chemicals Processes for Potentially Toxic Materials. Contract Number 68-03-2579. Environmental Protection Agency, Cincinnati, Ohio, August, 1978.
5. STANDARD INDUSTRIAL CLASSIFICATION MANUAL
Executive Office of the President / BUREAU OF THE BUDGET,
1976. pp 615.
6. Dorigan, J., Fuller, B. and R. Duffy. Scoring of Organic Air Pollutants Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals. Contract Number 68-02-1495, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1976. 331 pp.
7. Fairchild, E. J. Registry of Toxic Effects of Chemical Substances. Contract Number 210-75-0034, U.S. Dept. of Health, Education and Welfare. 1977 edition.
8. U.S. EPA Wastewater Treatability Manual, draft
Monsanto Research Corp. 1979.
9. State and Region NPDES permit files.

PRESURVEY DATA SHEETS

I. NAME OF COMPANY C150D DATE OF SUMMARY _____

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

_____ PHONE _____

EPA PERSONNEL _____ PHONE _____

_____ PHONE _____

STATE PERSONNEL _____ PHONE _____

_____ PHONE _____

INDUSTRY TYPE Municipal Sewage Treatment

PORTION OF PROCESS TO BE SAMPLED Outfall 001

II. PROCESS DESCRIPTION PRIMARY SEWAGE Treatment

II. Con't.

Raw materials and amounts _____

Fuels _____

Products and amounts _____

Operating Cycle:

Check: Batch _____ Continuous / Cyclic _____

Timing of batch or cycle _____

Best time to sample 8:00 AM TO 5:00 PM

Length of Operating day 24 HRS

Length of operating week 7 DAYS

Scheduled shutdowns N/A

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: INFLUENT, ALUM

ADDITION, GRT CHAMBER, POLYMER
ADDITION, PRIMARY SETTLING, CHLORINATION

Chemicals added and amounts Alum 1400 lbs/day; Polymer 30 lbs/day

Handles rainfall runoff? NO (ONLY NORMAL INFILTRATION)

Includes sanitary waste, flow YES 2.1 MGD

Source of plant intake water _____

Hydraulic retention time: Thru plant 1.15 HRS.
Thru treatment
unit operations _____

Recent treatment plant performance _____

III. Con't.

NPDES permit parameters and limits BOD₅ 140/210 TSS
100/150 FICAL 20/400 PH 6.0 TO 9.0 Cl. 1.

Final effluent flow rate _____ 2.

List of potential pollutants LINDANE, Chlorine

Recent analyses available? _____

Sampling point description CHLORINE CONTACT
TANK EFFLUENT

Use automatic sampler? Grab Sample

Electricity available YES

Extension cord and type of outlet? 100 FT

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions _____
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? NO
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location NORFOLK GENERAL
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

A. Plant Requirements I.D. CARD

Special time constraints: 0800 - 1700

B. MRC Agreement _____

C. Potential Problems _____

VI. SAMPLING HANDLING

A. Ice availability No

B. Sample splitting requested

Describe

C. Nearest airport: Norfolk International

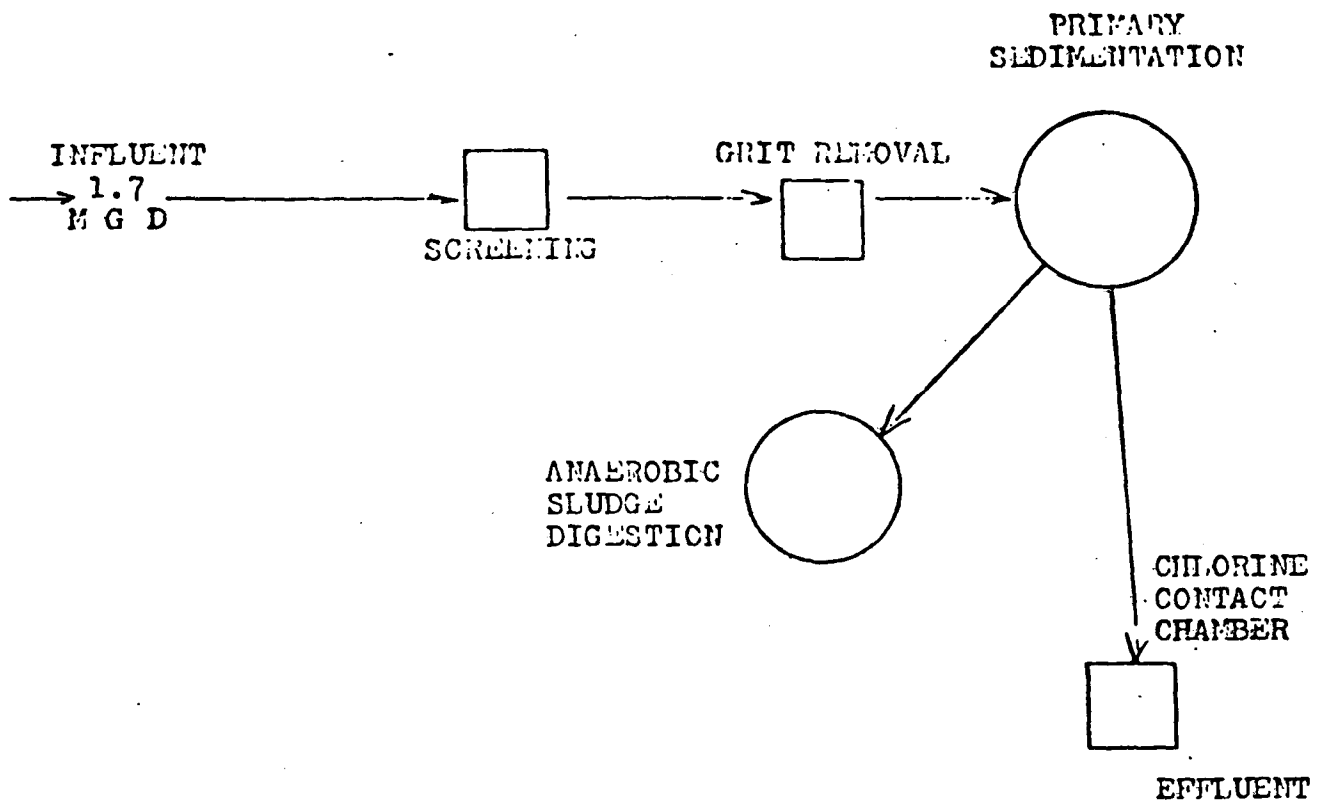
D. Chemical available: H_2SO_4

HNO_3

$NaOH$

VIL Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		



PRESURVEY DATA SHEETS

I. NAME OF COMPANY C155D DATE OF SUMMARY 5/11/81
ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

PHONE _____

EPA PERSONNEL _____ PHONE _____

PHONE _____

STATE PERSONNEL _____ PHONE _____

PHONE _____

INDUSTRY TYPE Sewage Treatment (Municipal)

PORTION OF PROCESS TO BE SAMPLED Outfall 001 final effluent
JUNCTION CHAMBER

II. PROCESS DESCRIPTION Primary Sewage Treatment /
Chemical addition

II. Con't.

Raw materials and amounts _____

Fuels _____

Products and amounts _____

Operating Cycle:

Check: Batch _____ Continuous ☒ Cyclic _____

Timing of batch or cycle N/A

Best time to sample 0800 to 1700

Length of Operating day 24 hrs.

Length of operating week 7 days

Scheduled shutdowns N/A

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: GRIT REMOVAL / PRIMARY

settling (floatation AND conventional) chlorination;
sludge holding - sludge thickening - incineration

Chemicals added and amounts 429 lbs/day POLYMER (Nalco 8773) Chlorine = 2600 lbs/day
Alum 15,609 lbs/day

Handles rainfall runoff? YES

Includes sanitary waste, flow YES

Source of plant intake water _____

Hydraulic retention time: Thru plant 2.3 hrs.
Thru treatment
unit operations _____

Recent treatment plant performance Refer to Summaries

III. Con't.

NPDES permit parameters and limits BOD₅ = 18,360 lbs/day 100 mg/l (monthly avg.)
TSS = 14,688 lbs/day (avg) 80 mg/l (monthly avg), pH 6.0-9.0, Total Col. = 1000 ntu avg 2000 max.

Final effluent flow rate 18.78 MGD

List of potential pollutants Possible cyanide (CN),
ZINC, CHLORODANE.

Recent analyses available? Refer to summaries

Sampling point description Final effluent junction
chamber (need 100 foot pump tubing)

Use automatic sampler? GRAB Sample

Electricity available YES

Extension cord and type of outlet? 100FT. (CR)

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions _____
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? NO
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location HAMPTON General
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

A. Plant Requirements I.D. CARD

Special time constraints: NONE

B. MRC Agreement _____

C. Potential Problems CONSTRUCTION WORK ON SITE

VI. SAMPLING HANDLING

A. Ice availability NOT AT SITE

B. Sample splitting requested _____

Describe _____

C. Nearest airport: Patrick Henry

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VIL Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY C156D DATE OF SUMMARY 5/11/81
ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

PHONE _____
EPA PERSONNEL _____ PHONE _____

PHONE _____
STATE PERSONNEL _____ PHONE _____

PHONE _____
INDUSTRY TYPE Sewage Treatment (Municipal)

PORTION OF PROCESS TO BE SAMPLED Outfall 001

II. PROCESS DESCRIPTION Sewage Treatment - Primary w/ chemical
Addition, chlorination for disinfection
Influent, bar screen, Alum addition, grit removal,
polymer addition, primary settling, flotation,
disinfection.

II. Con't.

Raw materials and amounts _____

Fuels _____

Products and amounts _____

Operating Cycle:

Check: Batch _____ Continuous ☒ Cyclic _____

Timing of batch or cycle N/A

Best time to sample 0800 TO 1700

Length of Operating day 24 HRS.

Length of operating week 7 DAYS

Scheduled shutdowns N/A

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION:

Influent, bar screen, Alum addition, grit removal
polymer addition, primary settling, floatation,
disinfection

Chemicals added and amounts Alum = 2069 lbs/day (11/20/73) Polymer = 455 lbs/day Chlorine

Handles rainfall runoff? YES (some from downtown)

Includes sanitary waste, flow YES

Source of plant intake water N/A

Hydraulic retention time: Thru plant 2 hrs.
Thru treatment
unit operations _____

Recent treatment plant performance Refer to summaries

III. Con't.

NPDES permit parameters and limits BOD₅ = 25.03% lbs/day (AVG)
100 mg/l (monthly avg), TSS = 20,038 lbs/day (AVG), pH 6.0 to 9.0, Fecal Coli 2000 max/ AVG

Final effluent flow rate MGD

List of potential pollutants CYANIDE (CN) 0

Recent analyses available? Refer to summary sheets
AND DMR'S

Sampling point description Effluent junction box (from pump)
20 foot vertical pick-up

Use automatic sampler? GRAB Sample

Electricity available YES

Extension cord and type of outlet? 130 ft. EXT. CORD

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

<u>Item</u>	<u>Plant</u>	<u>MRC</u>	<u>Item</u>	<u>Plant</u>	<u>MRC</u>
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions _____
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? YES
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location Norfolk General - Hampton Blvd.
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

- A. Plant Requirements I.D. CARD
- _____

Special time constraints: ANYTIME

- B. MRC Agreement _____
- _____

- C. Potential Problems NONE
- _____

VI. SAMPLING HANDLING

A. Ice availability NOT AT SAMPLING SITE

B. Sample splitting requested _____

Describe _____

C. Nearest airport: Norfolk International

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VII Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY C157D DATE OF SUMMARY _____

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

EPA PERSONNEL _____ PHONE _____

STATE PERSONNEL _____ PHONE _____

INDUSTRY TYPE Production of Nylon Fiber

MANUF. NYLON 6 Resins + Fibers

PORTION OF PROCESS TO BE SAMPLED Outfall 001 + 002

NON-CONTACT COOLING WATER

II. PROCESS DESCRIPTION _____

Cooling Water - refer to Flow diagram

II. Con't.

Raw materials and amounts

Fuels

Products and amounts

Operating Cycle:

Check: Batch

Continuous

Cyclic

Timing of batch or cycle

N/A

SANITARY WASTE IS BATCH

Best time to sample

0800 to 1700

Length of Operating day

24 hrs

Length of operating week

7 days

Scheduled shutdowns

NONE

Other

III.

WASTEWATER TREATMENT PLANT DESCRIPTION:

Refer to Flow diagram

Chemicals added and amounts

Chlorine (trace) Along Cottrell

Handles rainfall runoff?

YES

Includes sanitary waste, flow

YES Periodically

Source of plant intake water

James River

Hydraulic retention time: Thru plant

N/A

Thru treatment
unit operations

45 min. to 1 hr.

Recent treatment plant performance

III. Con't.

NPDES permit parameters and limits TSS = 2,738 lbs/day (DAILY AVG)

Chlorine Residual = NO MORE THAN 27 samples/month shall exceed 1.5 to 2.5 mg/l

Final effluent flow rate N/A NO LIMIT

List of potential pollutants Ammonia, Chlorobim, Methylene Chloride,
1,1 Trichloroethane, Tetrachloroethylene, Trichloroethane, Benzene, Toluene, CARBON
Chlorobenzene, 2-chloro naphthalene, 1,2-dichlorobenzene, Ethylbenzene, Dichlorobromo methane, Dichlorodifluoro methane
Phenol, Naphthalene, Pentachlorophenol, Dimethyl phthalate, ANTHRACENE.
 Recent analyses available? Refer to SUMMARIES

Sampling point description 001 + 002 ARE STEAMS
(TIDALLY INFLUENCED)

Use automatic sampler? GRAB SAMPLE

Electricity available NO

Extension cord and type of outlet? N/A

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions NONE
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? YES
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location HOPEWELL Rt 10
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

- A. Plant Requirements I.D. CARD

Special time constraints: 0800 to 1700

- B. MRC Agreement _____

- C. Potential Problems NONE

VI. SAMPLING HANDLING

A. Ice availability _____

B. Sample splitting requested _____

Describe _____

C. Nearest airport: Byrd International Airport

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VIL Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY CIGID DATE OF SUMMARY 5/12/81
ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

EPA PERSONNEL _____ PHONE _____

STATE PERSONNEL _____ PHONE _____

INDUSTRY TYPE SEWAGE Treatment (Municipal)
PORTION OF PROCESS TO BE SAMPLED Outfall 001

II. PROCESS DESCRIPTION Primary sewage treatment
Plant

II. Con't.

Raw materials and amounts N/A

Fuels _____

Products and amounts N/A

Operating Cycle:

Check: Batch _____ Continuous ☒ Cyclic _____

Timing of batch or cycle N/A

Best time to sample 0800 - 1700

Length of Operating day 24 HRS.

Length of operating week 7 DAYS

Scheduled shutdowns NONE

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: BAR SCREENS,
G.R.T. COLLECTOR, 2 1/2' PARSHALL FLUME,
SEDIMENTATION TANKS, CHLORINE
CONTACT TANKS, OUTFALL
(SLUDGE DIGESTION)

Chemicals added and amounts LIME = 200 lbs/day / 2016 BC lbs/day / 1500 lbs/day
POLYMER / CHLORINE

Handles rainfall runoff? SOME

Includes sanitary waste, flow YES

Source of plant intake water N/A

Hydraulic retention time: Thru plant _____
Thru treatment _____
unit operations _____

Recent treatment plant performance REFER TO SUMMARY

III. Con't.

NPDES permit parameters and limits BOD₅ = 15,400 lbs/day (avg) 140 mg/l (daily av)
TSS = 11,000 lbs/day (avg) 100 mg/l (daily av), pH = 6.0 to 9.0, Fecal Coli. = 200 monthly, 400 weekly

Final effluent flow rate 15 MGD

List of potential pollutants Chlorine

Recent analyses available? _____

Sampling point description Chlorine Contact Tank
(20 FT DROP)

Use automatic sampler? GRAB Sample

Electricity available YES

Extension cord and type of outlet? 30 FT

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions _____
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? YES
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location NORFOLK GENERAL
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

A. Plant Requirements I.D CARD

Special time constraints: NONE

B. MRC Agreement _____

C. Potential Problems _____

VI. SAMPLING HANDLING

A. Ice availability No

B. Sample splitting requested _____

Describe _____

C. Nearest airport: NORFOLK INTERNATIONAL

D. Chemical available: H_2SO_4 _____

HNO₃ _____

NaOH

VIL Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY C164D DATE OF SUMMARY 5/11/81

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

_____ PHONE _____

EPA PERSONNEL _____ PHONE _____

_____ PHONE _____

STATE PERSONNEL _____ PHONE _____

_____ PHONE _____

INDUSTRY TYPE Sewage Treatment (Municipal)

PORTION OF PROCESS TO BE SAMPLED Outfall 001,

(FINAL GRATING AFTER CHLORINE
CONTACT TANK)

II. PROCESS DESCRIPTION ACTIVATED SLUDGE SEWAGE
TREATMENT PLANT

II. Con't.

Raw materials and amounts _____

Fuels _____

Products and amounts _____

Operating Cycle:

Check: Batch _____ Continuous ☒ Cyclic _____

Timing of batch or cycle N/A

Best time to sample 0500 TO 1700

Length of Operating day 24 HOURS

Length of operating week 7 DAYS

Scheduled shutdowns N/A

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: SCREENING

GRIT REMOVAL → PRIMARY CLARIFIERS
(PRIMARY SLUDGE THICKENER → (D) →
→ INCINERATOR ON RETURN TO AERATION) →
FINAL CLARIFIERS → CHLORINE CONTACT TANK

INFLUENT PARSHALL FLUME

Chemicals added and amounts CAOH = 16000 lbs/day Polymer (Percol 757) 150 lbs/day
Chlorine = 800 lbs/day Polymer (NACA 8162) = 700 lbs/day
NADH = 6000 lbs/day Ammonia 6000 lbs/day Ferric Chloride = 1500 lbs/day

Handles rainfall runoff? NO (ONLY NORMAL INFILTRATION)

Includes sanitary waste, flow YES

Source of plant intake water N/A

Hydraulic retention time: Thru plant 12-15 hours
Thru treatment
unit operations _____

Recent treatment plant performance REFER TO SUMMARY

III. Con't.

NPDES permit parameters and limits BOD₅ = 2,403 lbs/day (AVG) 30 mg/l
monthly avg., TSS = 2,403 lbs/day (AVG), pH = 6.0 to 9.0, Fecal coli. 200 monthly avg.

Final effluent flow rate 9.6 MGD

List of potential pollutants BREWERY WASTES (ORGANICS)
POSSIBILITY OF CN; Small Qty. of Lead, Chromium,
Magnesium, Potassium and Phenol.

Recent analyses available? YES

Sampling point description 001 FINAL GRATING
AFTER CHLORINE CONTACT TANK

Use automatic sampler? GRAB SAMPLE

Electricity available YES

Extension cord and type of outlet? 50 FT

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions _____
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? YES
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location WILLIAMSBURG GENERAL
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

- A. Plant Requirements I.D. CARD

- Special time constraints: NONE

- B. MRC Agreement _____

- C. Potential Problems NONE

VI. SAMPLING HANDLING

A. Ice availability No

B. Sample splitting requested _____

Describe _____

C. Nearest airport: PATRICK HENRY Airport

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VII Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY C 169 D DATE OF SUMMARY 5/14/81
ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

EPA PERSONNEL _____ PHONE _____

STATE PERSONNEL _____ PHONE _____

INDUSTRY TYPE SEWAGE TREATMENT (Municipal & Industrial)
PORTION OF PROCESS TO BE SAMPLED Outfall 001

II. PROCESS DESCRIPTION Secondary ACTIVATED SLUDGE
UNOX (O₂)

II. Con't.

Raw materials and amounts

~~N/A~~

Fuels

Products and amounts

~~N/A~~

Operating Cycle:

Check: Batch

Continuous

✓

Cyclic

Timing of batch or cycle

~~N/A~~

Best time to sample

ANYTIME

Length of Operating day

24 HRS.

Length of operating week

7 DAYS

Scheduled shutdowns

~~N/A~~

Other

III. WASTEWATER TREATMENT PLANT DESCRIPTION:

REFER TO FLOW DIAGRAM

Chemicals added and amounts

50-300 g/day
(Herculose) Polymer (Polycarbonate) (NALCO) Defoamer = 1500 g/day

Handles rainfall runoff?

YES (SOME)

Includes sanitary waste, flow

YES

Source of plant intake water

~~N/A~~

Hydraulic retention time; Thru plant

6-8 HRS.

Thru treatment unit operations

Recent treatment plant performance

REFER TO SUMMARIES

III. Con't.

NPDES permit parameters and limits BOD₅ = 12,510 lbs/day (Avg) 30 mg/l (monthly avg)
TSS = 20,850 lbs/day, 50 mg/l (monthly avg), Chlorine Residual 1.5 mg/l, pH = 6.0 to 9.5.

Final effluent flow rate 50 MGD

List of potential pollutants Cu, Cd, Chromium, CA, NA, Mg,
Phenols, Organics, Chloroform, Methylene Chloride

Recent analyses available? REFER TO SUMMARIES & DMR'S

Sampling point description OPEN CHANNEL TROUGH

Use automatic sampler? GRAB SAMPLES

Electricity available YES

Extension cord and type of outlet? 25 ft.

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions NO smoking at UNOX
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? YES
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location _____
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

A. Plant Requirements I.D. CARD

Special time constraints: ANYTIME

B. MRC Agreement _____

C. Potential Problems NONE

VI. SAMPLING HANDLING

A. Ice availability _____

B. Sample splitting requested _____

Describe _____

C. Nearest airport: Hopewell (small)

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VII. Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY B142 S DATE OF SUMMARY _____
ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL Stephen Wilson and Tom Miller PHONE _____

PHONE _____

EPA PERSONNEL _____ PHONE _____

PHONE _____

STATE PERSONNEL _____ PHONE _____

PHONE _____

INDUSTRY TYPE Industrial waste treatment and recovery (SIC 4953)

PORTION OF PROCESS TO BE SAMPLED Outfall 002 - Treatment lagoon overflow

II. PROCESS DESCRIPTION Batch chemical treatment of waste by-products. Recovery of by-products for sale. (See attached sheets)

II. Con't.

Raw materials and amounts Waste acid solutions, chemicals, etc.

Fuels N.A.

Products and amounts N.A.

Operating Cycle:

Check: Batch ✓ Continuous _____ Cyclic _____

Timing of batch or cycle 1.5-2.0 hours

Best time to sample When discharge is occurring

Length of Operating day 16 hours

Length of operating week 6 days

Scheduled shutdowns None

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: Gravity settling
with batch discharge. (See diagram)

Chemicals added and amounts lime, Fe_2SO_4 , Na_2SO_4

Handles rainfall runoff? Yes, only from operational area

Includes sanitary waste, flow No

Source of plant intake water City water

Hydraulic retention time: Thru plant N.A.

Thru treatment
unit operations Approx 3 days

Recent treatment plant performance Normal

III. Con't.

NPDES permit parameters and limits pH (6.0-9.0), TSS (30 mg/l)
Cd (0.3 mg/l), Cr (0.5 mg/l), Hg (0.05 mg/l), Cu (1.5 mg/l), Pb (1.5 mg/l),
Ni (1.5 mg/l), Zn (1.5 mg/l)
 Final effluent flow rate 20 KGD for 10 days/month
 List of potential pollutants see attached list

Recent analyses available? Quarterly DMRs

Sampling point description Sample from cathwalk on
baggage in operation - after sample volume - gradient
gates

Use automatic sampler? Note: Batch discharge may
necessitate alteration of sample

Electricity available No - may be able to use extension

Extension cord and type of outlet? _____

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
Knee boots		✓	First aid		✓

B. SAMPLE SITE

1. Smoking restrictions None at site - note signs
2. Vehicle traffic rules Check with guard
3. Possible set-up/clean-up facilities? No
4. Evacuation procedures None
5. Alarms None
6. Hospital location Information available
7. Hospital Phone _____
- Emergency Numbers None

V. Plant Entry

- A. Plant Requirements Stop at guard and ask for appropriate personnel

Special time constraints: Set up with contact and guard.

- B. MRC Agreement None

- C. Potential Problems Rain and violent stream flow
Concern over newspapers (problem have occurred before)

VI. SAMPLING HANDLING

- A. Ice availability Local stores
- B. Sample splitting requested yes
Describe 1 set of volatile, 1 gal for organics, 1 gal for metals.
- C. Nearest airport: Information available
- D. Chemical available: H_2SO_4 _____
 HNO_3 _____
 $NaOH$ _____

VIL Field Test Schedule *Information available*

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday	<div>12/12/80</div>	
Saturday		

TREATMENT OF SPECIFIC BULK STREAMS

1. WATER FROM HCL SCRUBBER

- A. Average content - 10-30% HCL 1-2% HF
 B. Treatment - Add lime slurry to pH 8-8.5
 C. Reactions
 1. $2 \text{HCL} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2 \text{H}_2\text{O}$
 2. $2 \text{HF} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaF}_2 \downarrow + 2 \text{H}_2\text{O}$

2. SPENT ALUMINUM CHLORIDE ALKALATION CATALYST

- A. Average content - 5-20% HCL 10-25% AlCl_3
 B. Treatment - Add lime slurry to pH 7.5 - 8.0
 C. Reactions
 1. $2\text{HCL} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$
 2. $2\text{AlCl}_3 + 3 \text{Ca}(\text{OH})_2 \rightarrow 3 \text{CaCl}_2 + \text{Al}(\text{OH})_3 \downarrow$

3. HYDROCHLORIC ACID PICKLE LIQUOR

- A. Average content 10-20% HCL, 0.5 to 8.0% Fe, 0.1 - 3.0% Ni
 0-1 - 1.0% Cr
 B. Treatment - Add lime to pH 8.0 - 8.5 settle and decant
 If supernate contains nickle treat with lime
 to pH 10 - 10.5 or Na_2S settle and decant, Readjust
 pH to 8.0 - 8.5 before discharge
 C. Reactions
 1. $2\text{HCL} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$
 2. $\text{FeCl}_2 + 2\text{FeCl}_3 + 4 \text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2 \downarrow + 2\text{Fe}(\text{OH})_3 \downarrow + 4\text{CaCl}_2$
 3. $\text{NiCl}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ni}(\text{OH})_2 + \text{CaCl}_2$
 4. $2 \text{CrCl}_3 + 3 \text{Ca}(\text{OH})_2 \rightarrow 2 \text{Cr}(\text{OH})_3 \downarrow + 3\text{CaCl}_2$

4. NITRIC - HYDROCHLORIC PICKLE LIQUOR

- A. Average content - 0.2 - 24% HNO_3 , 0.01 - 5.0% HCL, 0.5 - 8.0% Fe
 0.1 - 3.0% Ni, 0.1 - 1.0% Cr.
Treatment - Add lime to pH 8.0 - 8.5 settle and decant
 If supernate contains nickle treat with lime to
 pH 10 - 10.5 or sodium sulfide settle and decant
 readjust pH to 8.0 - 8.5 before discharge
Reactions -
 1. $2\text{HNO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$
 2. $\text{Fe}^{++} + 2\text{Fe}^{+++} + 4\text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2 \downarrow + \text{Fe}(\text{OH})_3 + 4\text{Ca}^{++}$
 3. $\text{Ni}^{++} + \text{Cr}^{+++} + 4\text{Ca}(\text{OH})_2 \rightarrow \text{Ni}(\text{OH})_2 + \text{Cr}(\text{OH}) + 4\text{Ca}^{++}$

5. NITRIC - HYDROFLUORIC PICKLE LIQUOR

- A. Average content - 1 - 20% Nitric acid, 0.1 - 5% Hydrofluoric acid, 0.5 to 8.0% Fe, 0.1 - 3.0% Ni, 0.1 - 1.0% Cr
- B. Treatment - Add lime to pH 8.0 - 8.5 Settle and decant.
If supernate contains nickle treat with lime to pH 10 - 10.5 or sodium sulfide. Settle and decant
Readjust pH to 8.0 - 8.5 before discharge
- C. Reactions
1. $2\text{HNO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$
 2. $2\text{HF} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaF}_2\downarrow + 2\text{H}_2\text{O}$
 3. $\text{Fe}^{+2} + 2\text{Fe}^{+3} + 4\text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2\downarrow + \text{Fe}(\text{OH})_3 + 4\text{Ca}^{++}$
 4. $\text{Ni}^{++} + \text{Cr}^{+++} + 4\text{Ca}(\text{OH})_2 \rightarrow \text{Ni}(\text{OH})_2\downarrow + \text{Cr}(\text{OH})_3\downarrow + 4\text{Ca}^{++}$

6. SULFURIC ACID PICKLE LIQUOR

- A. Average content - 1 - 15% Sulfuric acid, 7 - 20% iron
- B. Treatment - Add lime slurry to pH 8.0 - 8.5
- C. Reactions
1. $\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_4\downarrow + 2\text{H}_2\text{O}$
 2. $\text{FeSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2\downarrow + \text{CaSO}_4\downarrow$

7. SULFURIC - HYDROCHLORIC PICKLE LIQUOR

- A. Average content - 10 - 15% hydrochloric, 1 - 2% sulfuric 3 - 5% iron, 4 - 6% copper
- B. Treatment - Lime slurry to pH 8.0 - 8.5 settle and decant
If supernate contains copper treat with sodium sulfide, settle and decant, readjust pH to 8.0 - 8.5 before discharge
- C. Reactions
1. $2\text{HCl} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$
 2. $\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_4\downarrow + 2\text{H}_2\text{O}$
 3. $\text{Fe}^{++} + 2\text{Fe}^{+++} + 4\text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2\downarrow + \text{Fe}(\text{OH})_3\downarrow + 4\text{Ca}^{++}$
 4. $\text{Cu}^{++} + \text{Ca}(\text{OH})_2 \rightarrow \text{Cu}(\text{OH})_2 + \text{Ca}^{++}$
 5. $\text{Cu}(\text{NH}_4)^{++} + 2\text{Na}_2\text{S} + \text{Ca}(\text{OH})_2 \rightarrow \text{CuS}\downarrow + \text{CaS} + 4\text{Na} + 4\text{NH}_3\uparrow + 12\text{H}_2\text{O}$

8. CHROMIC - SULFURIC PLATING OR ANODIZING BATH

- A. Average Content - 1 - 5% chromic, 1 - 5 % sulfuric
- B. Treatment -
1. Add ferrous sulfate in quantity sufficient to provide excess Fe^{+2} .
 2. After Cr^{+6} reduction, add lime slurry to pH 8.0 - 8.5.
- C. Reactions
1. $2\text{H}_2\text{Cr}_2\text{O}_7 + 6\text{FeSO}_4 + 9\text{H}_2\text{SO}_4 \rightarrow 2\text{Cr}_2(\text{SO}_4)_3 + 3\text{Fe}_2(\text{SO}_4)_3 + 14\text{H}_2\text{O}$
 2. $\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_4\downarrow + 2\text{H}_2\text{O}$
 3. $\text{Cr}_2(\text{SO}_4)_3 + 8\text{Ca}(\text{OH})_2 \rightarrow 3\text{CaSO}_4\downarrow + 2\text{Cr}(\text{OH})_3\downarrow$
 4. $\text{Fe}^{++} + 2\text{Fe}^{+++} + 4\text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2\downarrow + \text{Fe}(\text{OH})_3\downarrow + 4\text{Ca}^{++}$

9. CHROMIC - NITRIC DEOXIDIZER BATH

A. Average Content - 10 - 15% chromic acid, 10 - 15% nitric acid

B. Treatment

1. Add ferrous sulfate in quantity sufficient to provide an excess.
2. Add lime slurry to pH 8.0 - 8.5.

C. Reactions

1. $\text{H}_2\text{Cr}_2\text{O}_7 + 3\text{FeSO}_4 + 9\text{HNO}_3 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + 3\text{Fe}(\text{NO}_3)_3 + 7\text{H}_2\text{O}$
2. $2\text{HNO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$
3. $\text{Cr}_2(\text{SO}_4)_3 + 3\text{Ca}(\text{OH})_2 \rightarrow 2\text{Cr}(\text{OH})_3\downarrow + 3\text{CaSO}_4\downarrow$
4. $\text{Fe}^{+2} + \text{Fe}^{+3} + 4\text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2\downarrow + \text{Fe}(\text{OH})_3 + 4\text{Ca}^{++}$

10. COPPER AMMONIUM PERSULFATE ETCH

A. Average content - 1 - 10% ammonium sulfate, 1- 5% copper

B. Treatment - Add ferrous sulfate - sulfuric acid or $\text{Ca}(\text{OH})_2$ to pH 4.0 - 5.0. Add sodium sulfide in quantity sufficient to provide slight excess. Add lime slurry to pH 8.0 - 8.5.

C. Reactions

1. $\text{Cu}(\text{NH}_3)_4\text{SO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{Fe}(\text{OH})\downarrow + 2(\text{NH}_4)_2\text{SO}_4$
2. $\text{CuSO}_4 + \text{Na}_2\text{S} \rightarrow \text{CuS}\downarrow + \text{Na}_2\text{SO}_4$
3. $(\text{NH}_4)_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{NH}_3\downarrow + \text{CaSO}_4\downarrow + 2\text{H}_2\text{O}$

11. COPPER EDTA AMMONIUM PERSULFATE CLEANING SOLUTION

A. Average content - 1 - 10% ammonium hydroxide, 1 - 2% EDTA, 1 - 2% copper, 1 - 5% iron, 1 - 10% ammonium sulfate.

B. Treatment

1. Add ferrous sulfate - sulfuric acid to reduce pH to 4.0 - 5.0
2. Add sodium sulfide in quantity sufficient to precipitate copper
3. Add acid or lime slurry to adjust pH to 8.0 - 8.5

C. Reactions

1. $\text{Cu-EDTA} + \text{FeSO}_4 \rightarrow \text{Fe-EDTA} + \text{CuSO}_4$
2. $\text{CuSO}_4 + \text{Na}_2\text{S} \rightarrow \text{CuS}\downarrow + \text{Na}_2\text{SO}_4$
3. $\text{FeSO}_4 + \text{Na}_2\text{S} \rightarrow \text{FeS}\downarrow + \text{Na}_2\text{SO}_4$
4. $(\text{NH}_4)_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{NH}_3\uparrow + \text{CaSO}_4\downarrow + 2\text{H}_2\text{O}$
5. $\text{Fe-EDTA} + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca-EDTA} + \text{Fe}(\text{OH})_2$

12. ZINC CYANIDE PLATING BATH

A. Average content - 1 - 3% zinc, 1 - 12% NaCN, 1 - 10% NaOH, 1 - 5% Na_2CO_3

B. Treatment - add dilute sulfuric acid and ferrous sulfate to reduce alkalinity, convert cyanide to + complex ferro-ferric cyanide, and precipitate zinc.

C. Reactions

1. $\text{Na}_2\text{Zn}(\text{CN})_4 + \text{H}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 \rightarrow 4\text{NaCN} + \text{ZnSO}_4 + \text{CO}_2\uparrow + \text{H}_2\text{O}$
2. $\text{FeSO}_4 + 6\text{NaCN} \rightarrow \text{Na}_4\text{Fe}(\text{CN})_6 + \text{Na}_2\text{SO}_4$
3. $\text{FeSO}_4 + \text{Na}_4\text{Fe}(\text{CN})_6 \rightarrow \text{Fe}_2\text{Fe}(\text{CN})_6\downarrow + 2\text{Na}_2\text{SO}_4$
4. $2\text{ZnSO}_4 + \text{Na}_4\text{Fe}(\text{CN})_6 \rightarrow \text{Zn}_2\text{Fe}(\text{CN})_6\downarrow + 2\text{Na}_2\text{SO}_4$

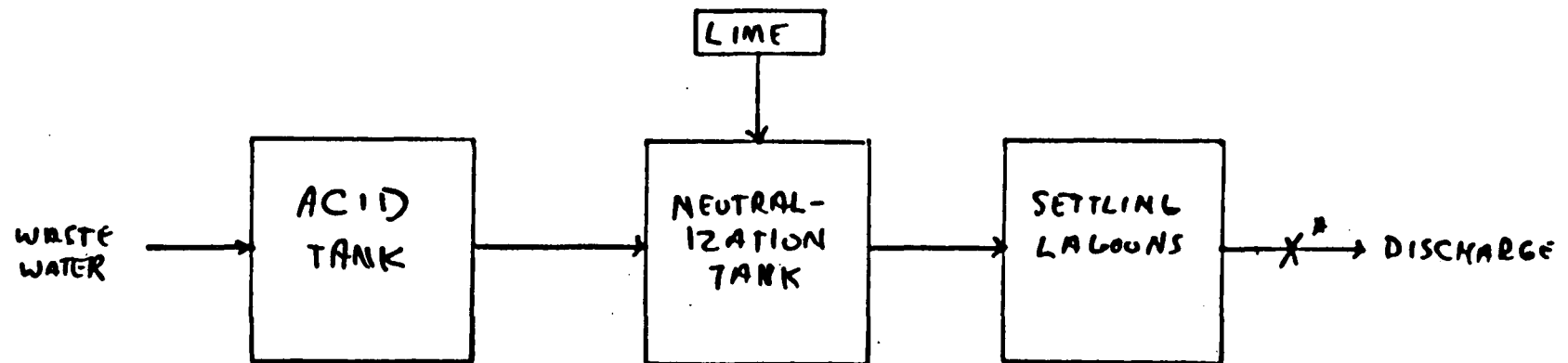
13. CADMIUM CYANIDE PLATING BATH

- A. Average content - 1 - 9% Cd, 1 - 12% NaCN, 1 - 10% NaOH
1 - 5% Na₂CO₃
- B. Treatment - Add dilute sulfuric acid and ferrous sulfate to reduce alkalinity and convert cyanides to complex ferro-ferricyanide and precipitate cadmium.
- C. Reactions
1. $\text{Na}_2\text{Cd}(\text{CN})_4 + \text{H}_2\text{SO}_4 + 2\text{Na}_2\text{CO}_3 \rightarrow \text{CdCO}_3\downarrow + \text{Na}_2\text{SO}_4 + 4\text{NaCN} + \text{CO}_2\uparrow$
 2. $\text{FeSO}_4 + 6\text{NaCN} \rightarrow \text{Na}_4\text{Fe}(\text{CN})_6 + \text{Na}_2\text{SO}_4$
 3. $2\text{FeSO}_4 + \text{Na}_4\text{Fe}(\text{CN})_6 \rightarrow \text{Fe}_2\text{Fe}(\text{CN})_6\downarrow + 2\text{Na}_2\text{SO}_4$
 4. $\text{CdSO}_4 + \text{Na}_4\text{Fe}(\text{CN})_6 \rightarrow \text{Cd}_2\text{Fe}(\text{CN})_6 + 2\text{Na}_2\text{SO}_4$

14. COPPER CYANIDE PLATING BATH

- A. Average content - 1 - 5% copper, 1 - 10% NaCN, 1 - 10% NaOH
- B. Treatment - Add dilute sulfuric acid and ferrous sulfate to reduce alkalinity, convert cyanide to complex ferro-ferricyanides and precipitated copper.
- C. Reactions
1. $\text{NaCu}(\text{CN})_3 + \text{H}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 \rightarrow 3\text{NaCN} + \text{CuSO}_4$
 2. $\text{FeSO}_4 + 6\text{NaCN} \rightarrow \text{Na}_4\text{Fe}(\text{CN})_6 + \text{Na}_2\text{SO}_4$
 3. $2\text{CuSO}_4 + \text{Na}_4\text{Fe}(\text{CN})_6 \rightarrow \text{Cu}_2\text{Fe}(\text{CN})_6 + 2\text{Na}_2\text{SO}_4$

PLANT 51425 W TE TREATMENT
WASTE TREATMENT AND RECOVERY



* Sample Collection Point

Justification for Toxic compound selection

An analysis of each production process was undertaken to evaluate those pollutants which could potentially be present in the process effluent. Emphasis was placed on pollutants potentially present due to production and/or subsequent wastewater treatment.

This analysis typically involved first a compilation of information from respective NPDES permit files. This information, yielding location, type or types of processes, general flow diagrams, etc., was then applied to the list of references for each preliminary report. These additional references yielded information regarding reactants, products, byproducts, general unit operations employed and their parameters, plant specific information where known, experience with similar plants or industries, and finally, actual wastewater characterization data for each industry type.

Possible pollutant sources in the process wastewaters included water as a product of combustion or other process reaction, direct contact cooling water, product wash water, reactor washout wastes, condenser and scrubber water which has contacted either products or reactants, non-contact cooling water which may be contaminated due to process flange leaks, etc and finally, pollutants which may be produced as a result of the wastewater treatment system unit operations.

The analysis protocol for Phase I calls for automatically monitoring NPDES parameters, phenol, cyanide, inorganic ions and 76 elemental compounds. Therefore, organic compounds are the major output of this exercise.

No formal consideration was given to possible background contamination, e.g. plant intake waters, as the program is concerned with the contribution emanating from a particular production point source.

The list of organic compounds finally generated was evaluated to determine the toxicity of its members.

As stated in the project work plan, those compounds suspected to be particularly toxic are to be semi-quantified, whenever possible, with the remainder of the list scanned for via mass spectrometry.

The toxicity evaluation parameters were as follows:

Any lethality rating < 500 mg/kg	→ semi-quantify
Any identified carcinogenicity	→ semi-quantify
Any identified mutagenicity	→ semi-quantify
Any identified teratogenicity	→ semi-quantify
Any known toxic decomposition products	→ semi-quantify
None of the above	→ qualify via M. S.

Plant B1425 is engaged in the neutralization of waste chemical solutions and compounds. A major process contributor is spent solutions from acid-gas scrubbers. All known input streams for this and other neutralization schemes within the plant are inorganic in nature. Therefore, no chromatographical organics are expected.

B 1425
SUSPECTED POLLUTANTS

No. Chromatographable Organics expected.

All sampling and testing methods for the plant are anticipated to be identical to those outlined in the project work plan, dated 26 November, 1979. Any deviations are noted herein.

References

1. Gerstle, R., and J. Richards. Industrial Process Profiles for Environmental Use. EPA-600/2-77-023d, U.S. Environmental Protection Agency, Cincinnati, OHIO, February 1977.
2. Letkiewicz F. Chemicals Which Have Been Tested for Neurotoxic Effects. EPA-560/1-76-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1976. 1332 pp.
3. Markle, R.A., Fentiman, A.F., Steadman, T.R. and R.A. Mayer. An Assessment of the Treatment and Control of Wastes From the Manufacture and Use of Potentially Toxic and Hazardous Organic Chemicals. U.S. Environmental Protection Agency (Zettelle Columbus Laboratories Contract Number 68-02-1323). Cincinnati, OHIO, June 1974. 290 pp.

4. Watkins, DR. Review of Industrial Organic Chemicals Processes for Potentially Toxic Materials. Contract Number 68-03-2579. Environmental Protection Agency, Cincinnati, Ohio, August, 1978.
5. STANDARD INDUSTRIAL CLASSIFICATION MANUAL, Executive Office of the President / BUREAU OF THE BUDGET, 1976. pp 615.
6. Dorigan, J., Fuller, B. and R. Duffy. Scoring of Organic Air Pollutants Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals. Contract Number 68-02-1495, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1976. 331 pp.
7. Fairchild, E. J. Registry of Toxic Effects of Chemical Substances. Contract Number 210-75-0034, U.S. Department of Health, Education and Welfare. 1977 edition.
8. Merck and Co., The Merck Index 9th Edition, 1976.

PRESURVEY DATA SHEETS

I. NAME OF COMPANY B1495 DATE OF SUMMARY _____

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL David Dunn and David Vane PHONE (513) - 268-3411

PHONE _____

EPA PERSONNEL _____ PHONE _____

PHONE _____

STATE PERSONNEL _____ PHONE _____

PHONE _____

INDUSTRY TYPE Manufacture of stainless steel plates, strip, sheet and bars (SIC 3312)

PORTION OF PROCESS TO BE SAMPLED Outfall 001 - total process effluent

II. PROCESS DESCRIPTION Manufacture of stainless steel bars, plates, sheet and strips from purchased scrap and ferro alloys including melting, rolling and finishing operations (see diagram)

II. Con't.

Raw materials and amounts Stainless steel scrap, carbon scrap, Ni, Cr

Fuels Natural gas, #2 fuel oil, propane

Products and amounts Stainless steel (3)

Operating Cycle:

Check: Batch _____ Continuous ✓ Cyclic _____

Timing of batch or cycle _____

Best time to sample Any 24 hour period (7 a.m. - midnight but 2 pickling)

Length of Operating day 24 hours

Length of operating week 6 days (6 1/2 for some operations)

Scheduled shutdowns July 3 - July 20

Other May shut down early (June 28). Also shutdown on bad days

III. WASTEWATER TREATMENT PLANT DESCRIPTION: Sanitary sewer, sent to

county sanitary sewers. Only wastes are segregated, skimmed and removed from plant by a vendor. Weak acid waste is sent to lagoons for neutralization with dolomite lime slurry. Spent pickle liquor is removed by a vendor (see diagram)

Chemicals added and amounts Polymers (Hexamer, Hexamer 847), high Ca

Handles rainfall runoff? Yes

Includes sanitary waste, flow No

Source of plant intake water City water, wells

Hydraulic retention time: Thru plant 3-4 hours

Thru treatment
unit operations 4 hours

Recent treatment plant performance 3-4 times per some acid tanks may overflow into waste water system

III. Con't.

NPDES permit parameters and limits TSS(105 lb/day), Fe(42 #/day)
Cr(3.1 #/day), Hex Cr(0.01 #/day), Ni(2.1 #/day), F(84 #/day)

Final effluent flow rate 0.7 MGD (dry weather average)

List of potential pollutants See attached list

Recent analyses available? No

Sampling point description Sampled overflow from Agrow
(2000-3000 feet from actual outfall). Very limited space

Dis collector container 10-15 ft from overflow. Request flow by metering
thru chest when starting 24 hr period
 Use automatic sampler? No (may need to use batteries)

Electricity available _____

Extension cord and type of outlet? _____

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses	✓	✓	Dust masks		
Goggles			Vapor masks		
Side shields	✓	✓	Air purifying		
Face shields			Air supply		
Hard hats	✓	✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes	✓	✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid	✓	✓

A. SAMPLE SITE

1. Smoking restrictions None
2. Vehicle traffic rules 10 mph. Obtain special truck pass at guard house
3. Possible set-up/clean-up facilities? Instrument shops or WWTP
4. Evacuation procedures No problem
5. Alarms None (sirens)
6. Hospital location Information available
7. Hospital Phone _____
- Emergency Numbers Guard house -331, 301; Fire-222

V. Plant Entry

- A. Plant Requirements Sign in at guard house and obtain truck pass

Special time constraints: None (wastewater operator might escort)

- B. MRC Agreement No

- C. Potential Problems With sampling date

VI. SAMPLING HANDLING

A. Ice availability Local stores

B. Sample splitting requested yes

Describe 1 gal from 55 gal sample to be split for
for NPDC's parameter analysis

C. Nearest airport: Information available

D. Chemical available: H_2SO_4

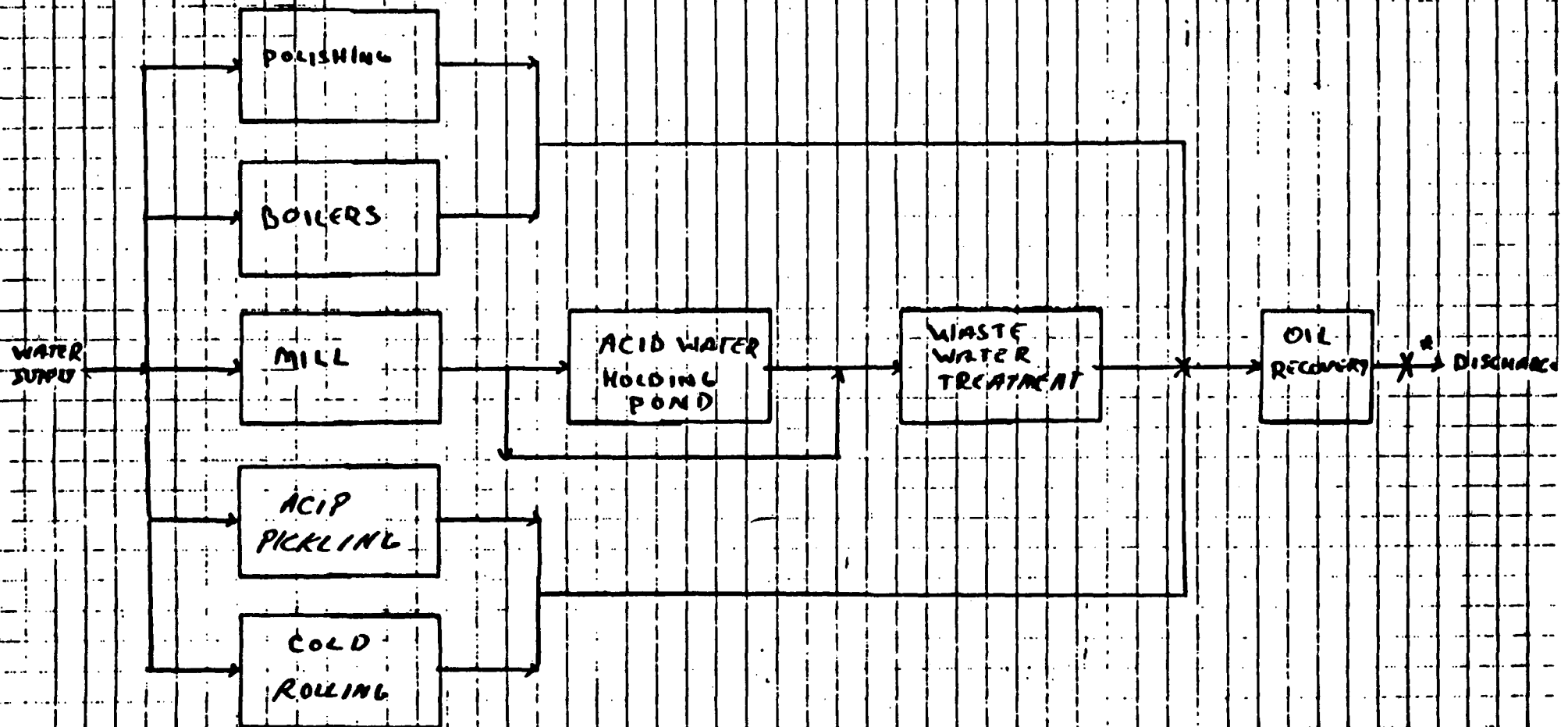
HNO_3

$NaOH$

VII. Field Test Schedule *Information available*

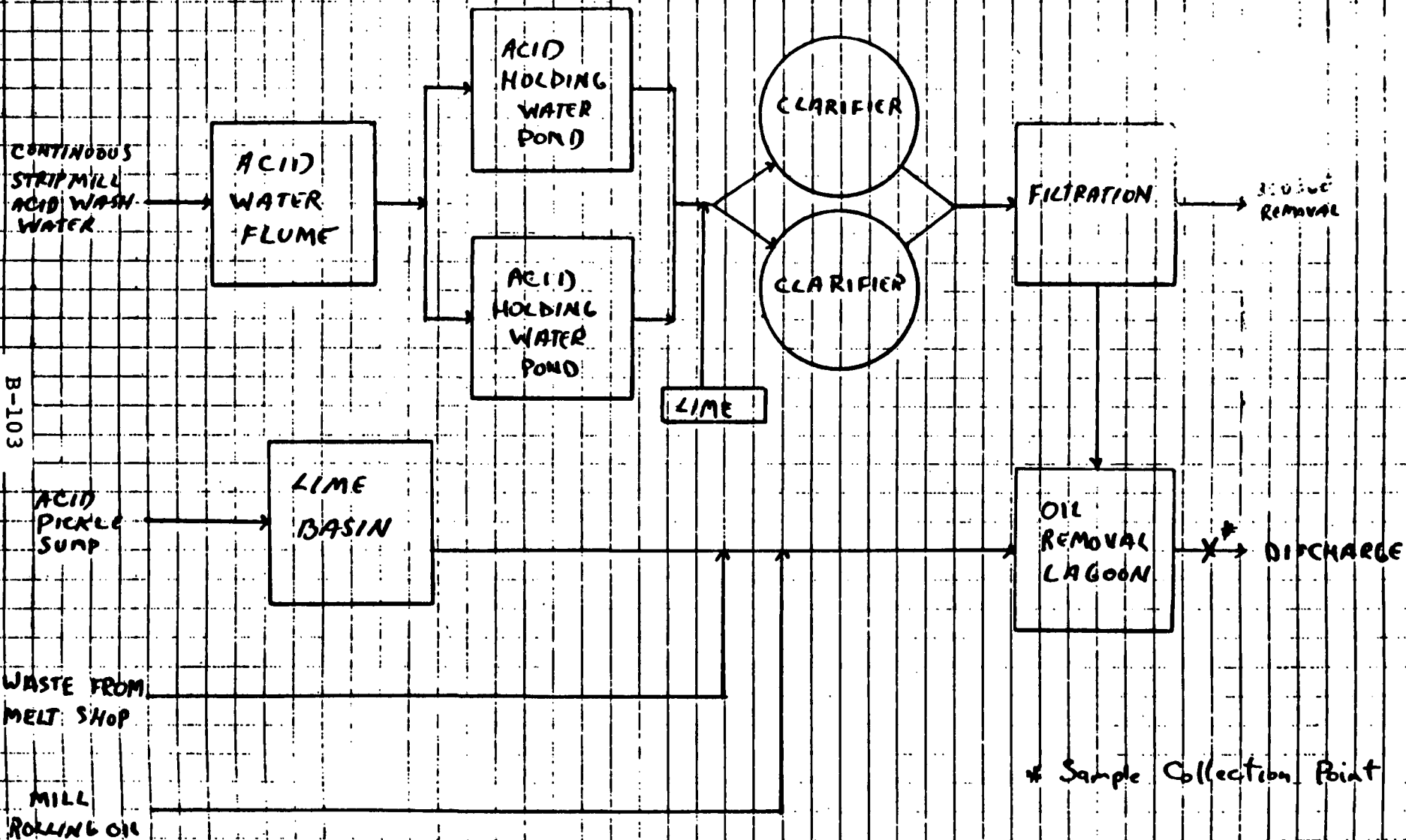
<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PLANT B1495 WATER FLOW
STAINLESS STEEL PRODUCTION



* Sample Collection Point

PLANT B149 S WASTE TREATMENT



* Sample Collection Point

Justification for Toxic compound selection

An analysis of each production process was undertaken to evaluate those pollutants which could potentially be present in the process effluent. Emphasis was placed on pollutants potentially present due to production and/or subsequent wastewater treatment.

This analysis typically involved first a compilation of information from respective NPDES permit files. This information, yielding location, type or types of processes, general flow diagrams, etc., was then applied to the list of references for each presurvey report. These additional references yielded information regarding reactants, products, byproducts, general unit operations employed and their parameters, plant specific information where known, experience with similar plants or industries, and finally, actual wastewater characterization data for each industry type.

Possible pollutant sources in the process wastewaters included water as a product of combustion or other process reaction, direct contact cooling water, product wash water, reactor washout wastes, condenser and scrubber water which has contacted either products or reactants, non-contact cooling water which may be contaminated due to process flange leaks, etc and finally, pollutants which may be produced as a result of the wastewater treatment system unit operations.

The analysis protocol for Phase I calls for automatically monitoring NPDES parameters, phenol, cyanide, inorganic ions and 76 elemental compounds. Therefore, organic compounds are the major output of this exercise.

No formal consideration was given to possible background contamination, e.g. plant intake waters, as the program is concerned with the contribution emanating from a particular production point source.

The list of organic compounds finally generated was evaluated to determine the toxicity of its members.

As stated in the project work plan, those compounds suspected to be particularly toxic are to be semi-quantified, whenever possible, with the remainder of the list scanned for via mass spectrometry.

The toxicity evaluation parameters were as follows:

Any lethality rating < 500 mg/kg	→	semi-quantify
Any identified carcinogenicity	→	semi-quantify
Any identified mutagenicity	→	semi-quantify
Any identified teratogenicity	→	semi-quantify
Any known toxic decomposition products	→	semi-quantify
None of the above	→	qualify via M. S.

Plant B1495 is engaged in manufacturing stainless steel strip and plates, etc. Experience has indicated that the compounds on the list are generally typical to the steel production industry.

B1495
SUSPECTED POLLUTANTS

Carbon tetrachloride*

1,1,1-Trichloroethane

Chloroform*

Chlorophenol*

2,4-Dichlorophenol*

Ethylbenzene

Pentachlorophenol*

Phenol*

Tetrachloroethylene*

Toluene*

Xylene*

Benzene*

*To be semi-quantified due to potential toxicity, carcinogenicity,
mutagenicity or teratogenicity.

All sampling and testing methods for the plant are anticipated to be identical to those outlined in the project work plan, dated 26 November, 1979. Any deviations are noted herein.

References

1. Gerstle, R., and J. Richards. Industrial Process Profiles for Environmental Use. EPA-600/2-77-023d, U.S. Environmental Protection Agency, Cincinnati, OHIO, February 1977.
2. Letkiewicz F. Chemicals Which Have Been Tested for Neurotoxic Effects. EPA-560/1-76-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1976. 1332 pp.
3. Markle, R.A., Fentiman, A.F., Steadman, T.R. and R.A. Mayer. An Assessment of the Treatment and Control of Wastes From the Manufacture and Use of Potentially Toxic and Hazardous Organic Chemicals. U.S. Environmental Protection Agency (Battelle Columbus Laboratories Contract Number 68-02-1323). Cincinnati, OHIO, June 1974. 290 pp.

4. Watkins, M.R. Review of Industrial Organic Chemicals
Processes for Potentially Toxic Materials. Contract Number
68-03-125-88. Environmental Protection Agency, Cincinnati,
Ohio, August, 1978.

5. STANDARD INDUSTRIAL CLASSIFICATION MANUAL,
Executive Office of the President, BUREAU of the Budget,
1976. pp 615.

6. Porigan, J., Fuller, B. and R. Duffy. Survey of Organic
Air Pollutants Chemistry, Prediction and Toxicity of
Selected Synthetic Organic Chemicals. Contract Number
68-C-2-1475, U.S. Environmental Protection Agency, Cincinnati,
Ohio, September-1976. 331 pp.

7. Fairchild, E. J., Registry of Toxic Effects of Chemical
Substances. Contract Number 210-75-0034, U.S. Department
of Health, Education and Welfare. 1977 edition.

8. Merck and Co., The Merck Index 9th edition, 1976.

9. Draft Development Document for the Iron and Steel Manufacturing Point Source Category, Effluent Guidelines Division, Office of Water and Waste Management, U.S. Environmental Protection Agency, October, 1979.

PRESURVEY DATA SHEETS

I. NAME OF COMPANY # A 101 DATE OF SUMMARY _____

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL Stephen Wilson PHONE 513-268-3411

David Dunn PHONE 513-268-3411

EPA PERSONNEL _____ PHONE _____

_____ PHONE _____

STATE PERSONNEL _____ PHONE _____

_____ PHONE _____

INDUSTRY TYPE Synthetic fibers

PORTION OF PROCESS TO BE SAMPLED outfall 101, total process effluent

II. PROCESS DESCRIPTION (SEE ATT.) _____

II. Con't.

Raw materials and amounts _____

Fuels #6 oil

Products and amounts SEE NPDES Application

Operating Cycle:

Check: Batch _____ Continuous ✓ Cyclic _____

Timing of batch or cycle _____

Best time to sample ANYTIME

Length of Operating day 24 hrs

Length of operating week 7 days

Scheduled shutdowns NONE

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: SEE figures

Chemicals added and amounts NaOH, H₂SO₄

Handles rainfall runoff? SOME

Includes sanitary waste, flow yes, 30,000 gpd

Source of plant intake water Deep Wells & city

Hydraulic retention time: Thru plant _____

Thru treatment
unit operations 1-1.5 days

Recent treatment plant performance Normal

III. Con't.

NPDES permit parameters and limits BOD (560 #/d)
COD (1000 #/d), Zn (10 #/d)

Final effluent flow rate 625,000 gpd

List of potential pollutants SEE ATTACHMENT

Recent analyses available? SEE DMRs

Sampling point description SAMPLE THRU GRATING ABOVE
FIRE POND. Pull grabs FROM exit of parshall flume

Use automatic sampler? yes

Electricity available yes

Extension cord and type of outlet? 6 ft., 3 prong

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions NO
2. Vehicle traffic rules 15 mph
3. Possible set-up/clean-up facilities? SEE PLANT CONTACT
4. Evacuation procedures SEE TREATMENT OPERATOR IF
OCURS
5. Alarms —
6. Hospital location —
7. Hospital Phone SEE phone book
Emergency Numbers ON-SITE FIRST AID AVAILABLE

V. Plant Entry

- A. Plant Requirements CALL PLANT CONTACT FROM GUARDHOUSE

Special time constraints: SEE PLANT CONTACT

- B. MRC Agreement NO CAMERAS, DON'T GO ROAMING
AROUND THE PLANT

- C. Potential Problems —

VI. SAMPLING HANDLING

- A. Ice availability SEE PLANT CONTACT
- B. Sample splitting requested yes
Describe 1/2 gal. they will supply container for
organics
- C. Nearest airport: —
- D. Chemical available: ~~H₂SO₄~~ _____
~~HNO₃~~ _____
~~NaOH~~ _____

A101

Compounds to be specifically

SEMQUANTIFIED

ACETONITRILE

BENZENE

Formaldehyde

Morpholine

Ethyl pyridine

2-Propenenitrile (Acrylonitrile)

Compounds to be
qualitatively scanned for

Acetic acid

Diethanol amine

Bromethane

Formic acid

2-Propanone (Acetone)

TO RECREATION AREA



RECEIVED

SAMPLE PT. 002

TO ROUTE 60

PARKING

PARKING

MAIN GATE

WOODED

CAFETERIA

201

202

PARKING

WOODED

WOODED

203

217

218

PARKING

208

209

210

211

228

227

229

230

RAIL ROAD

231

221

222

223

224

225

226

227

228

FUEL

OIL

STORAGE

232

233

TREATMENT

PLANT

SAMPLE

PT.

234

WASTE WATER
TREATMENT PLANT
LAGOONS

0 1 2 3 4 5
SCALE IN 100 FT

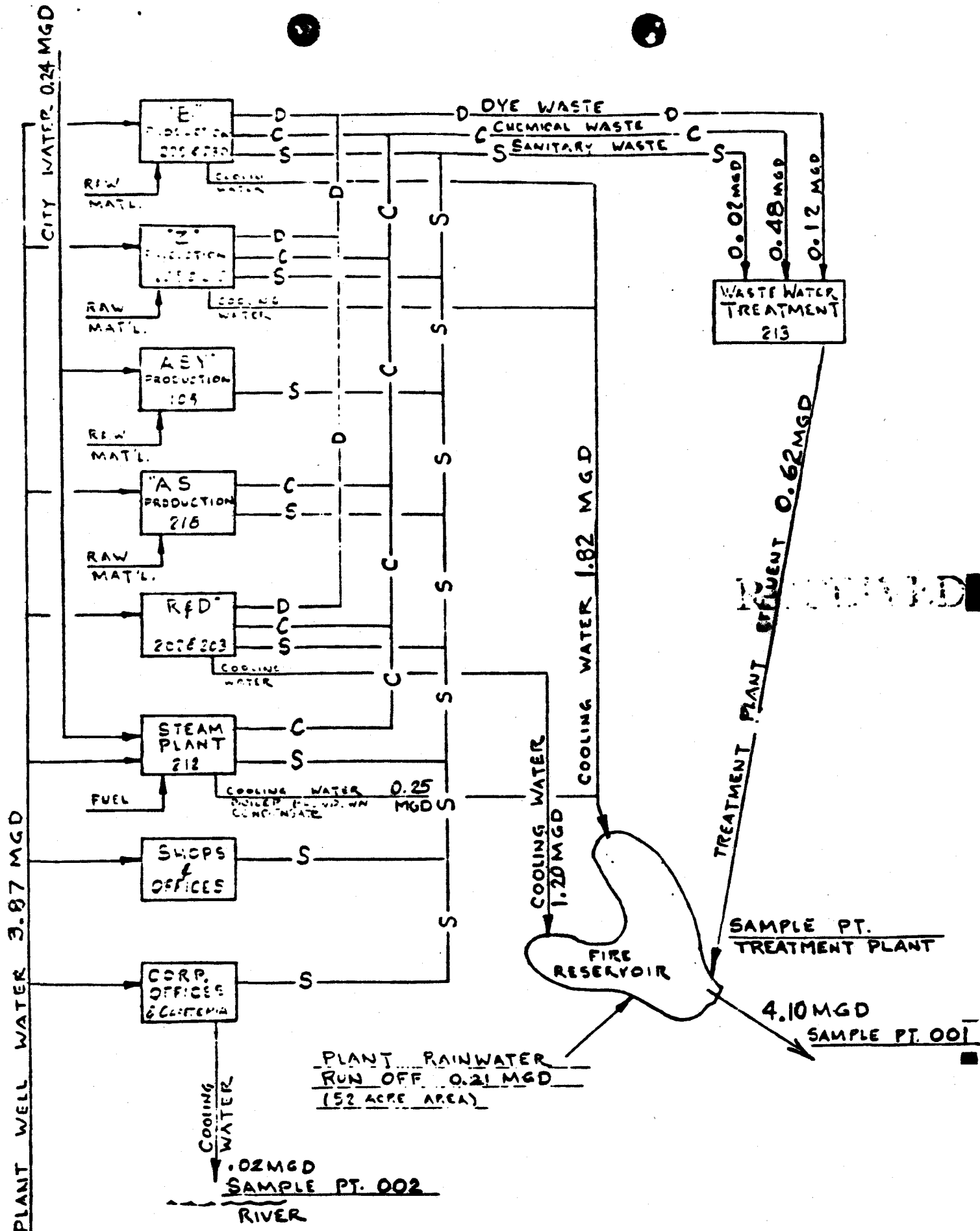
TO OIL
PIER

B-117

SAMPLE PT.
001

TO WOOD

JAMES RIVER



CHEMICAL WASTE 0.48 MGD

DYE WASTE
0.12 MGD

DYE
REMOVAL
CLARIFIER

EQUALIZATION
LAGOON #1

EQUALIZATION LAGOON #4

SLUDGE DRYING LAGOON

RECEIVE

MAR 5 1979

STATE WATER CONTROL BOARD
Hidewater Regional Office

CLARIFIER

CLARIFIER

SEDIMENTATION
LAGOON #2

SLUDGE
THICKNER

SEDIMENTATION
LAGOON #3

SANITARY
WASTE
0.02 MGD

TRICKLING FILTERS
SECONDARY CLARIFIERS

COOLING
WATER

RAIN 0.2 MGD

TREATMENT PLANT EFFLUENT 0.62 MGD

FIRE RESERVOIR

SAMPLE PT.

EFFLUENT 4.10 MGD

B-119

15

PRESURVEY DATA SHEETS

I. NAME OF COMPANY B.I.I.D. DATE OF SUMMARY _____
ADDRESS _____ PHONE _____
NAME OF CONTACTS Information Available
MRC PERSONNEL David Dunn PHONE (513) 268-3411
David Vanek PHONE _____
EPA PERSONNEL _____ PHONE _____
STATE PERSONNEL _____ PHONE _____
INDUSTRY TYPE SIC Code 2621, Tobacco Processing Facility
PORTION OF PROCESS TO BE SAMPLED Waste Treatment Plant Process Effluent

II. PROCESS DESCRIPTION _____
Manufactures all tobacco, wood pulp, and combination tobacco
and wood pulp sheets on paper machines. The Company's Research and Development
facility located on the same property has the capability of producing similar
products on an experimental paper machine.

II. Con't.

Raw materials and amounts	Tobacco	- 96 Tons/Day Maximum
	Wood Pulp	- 13 Tons/Day Maximum
	Activated Carbon	- 7 Tons/Day Maximum

Fuels Coal and Oil

Products and amounts	Tobacco Sheet	- 67 Tons/Day Maximum
	Paper Sheet	- 14 Tons/Day Maximum

Operating Cycle:

Check: Batch _____ Continuous _____ Cyclic X
Plant operates 24 hours/day for 10 days and shut
Timing of batch or cycle down for 4 days. Cycle repeats every 2 weeks.

Best time to sample During last 5 days of 10-day operating period.

Length of Operating day 24 Hours

Length of operating week Equivalent 5 days each week

Scheduled shutdowns * Saturday, Sunday, Monday, and Tuesday every other week

Other Weeks of July 4 and Christmas

** See Attached 1980 Operating Schedule*

III. WASTEWATER TREATMENT PLANT DESCRIPTION: _____

The sanitary waste discharges to a stabilization pond, and the discharge is
chlorinated prior to being mixed with the industrial discharge. Industrial
wastewater facilities consist of a primary clarifier, two aeration lagoons, and
a secondary clarifier with activated sludge returned to the aeration lagoons.

Chemicals added and amounts Chlorine (sanitary waste only) - 14 Pounds/Day

Handles rainfall runoff? No

Includes sanitary waste, flow 10,000 gpd sanitary treated separately and
combined with process at outfall

Source of plant intake water Texas River and County Water System

Hydraulic retention time: Thru plant 12.6 days

Thru treatment

unit operations Primary Clarifier - 0.3 Days,

Aeration Lagoons - 11.9 Days, Secondary Clarifier - 0.4 Days

Recent treatment plant performance Nov. 1979 % Reduction - BOD 99.0%
Suspended Solids 96.9%

III. Con't.

NPDES permit parameters and limits BOD₅ (750# / day), TSS (300# / day),
pH (6.0 - 8.5), fecal coliform (200 / 100 ml monthly avg)

Final effluent flow rate Process 1.128 MGD - Sanitary 0.010 MGD

List of potential pollutants See attached sheet

Recent analyses available? _____

Sampling point description Discharge of parshall flume in open
channel - Outfall 001 - presently proposing sampling only process
stream due to exposure of sample site to surface runoff and
ground water (see attached diagram)
 Use automatic sampler? yes

Electricity available 110 Volt

Extension cord and type of outlet? Three prong twist lock

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

<u>Item</u>	<u>Plant</u>	<u>MRC</u>	<u>Item</u>	<u>Plant</u>	<u>MRC</u>
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓
			Flash light		✓

B. SAMPLE SITE

1. Smoking restrictions None in waste treatment areas
2. Vehicle traffic rules Drive carefully and observe posted regulations and signs (20 mph speed limit, stop signs, etc.)
3. Possible set-up/clean-up facilities? None at sampling location
4. Evacuation procedures Not defined in area of waste treatment
5. Alarms None in waste treatment areas
6. Hospital location Information available
7. Hospital Phone Information available
- Emergency Numbers _____

V. Plant Entry

- A. Plant Requirements Notify management of desire to enter and accompaniment by management representative.

Special time constraints: Normal office hours are 8:30 a.m. to 5p.m. weekdays.

- B. MRC Agreement _____

- C. Potential Problems Entry at hours other than normal office hours require management notification to allow scheduling of management representative to be at location.

VI. SAMPLING HANDLING

- A. Ice availability see local store
- B. Sample splitting requested _____
Describe _____

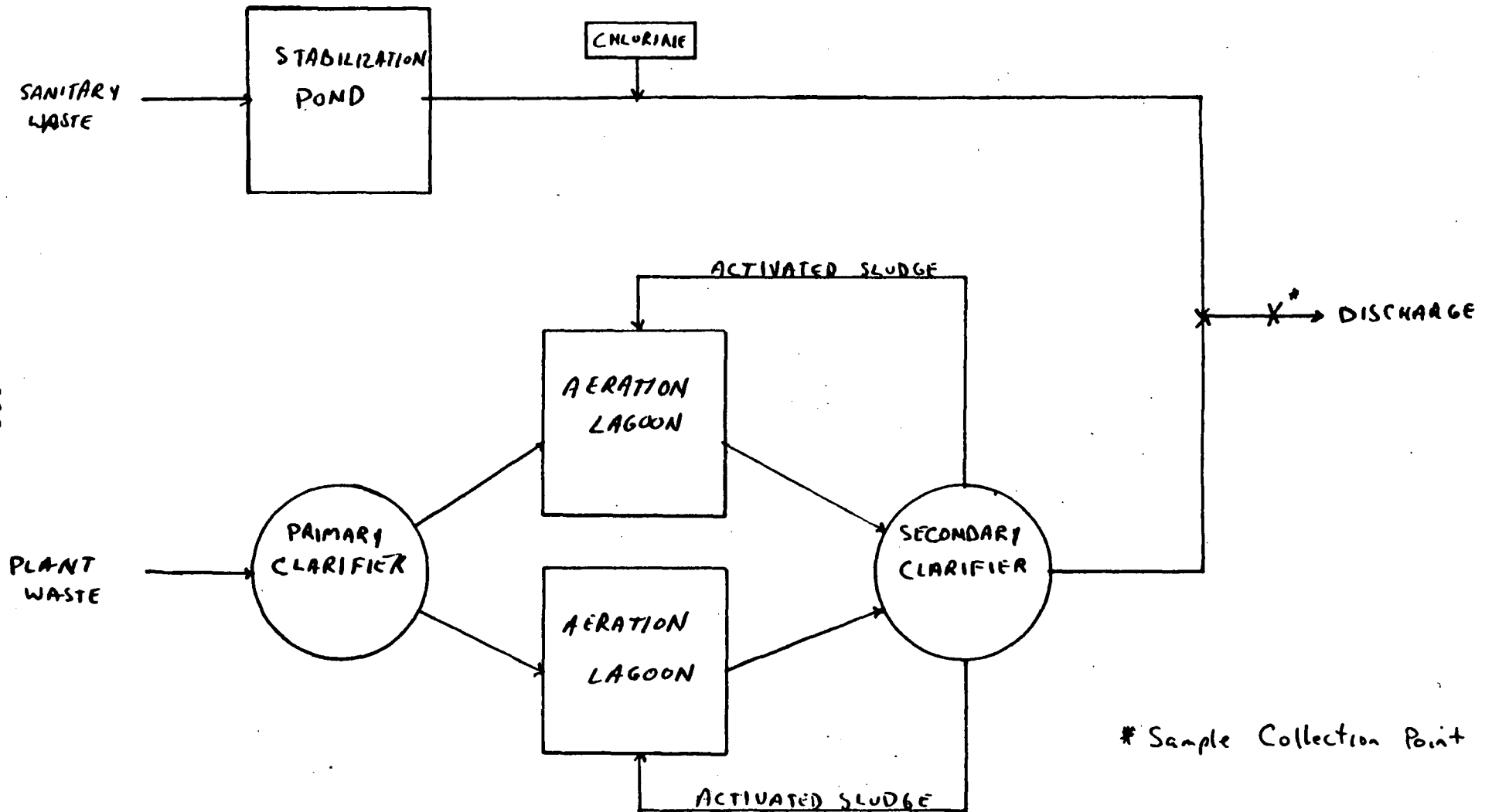
- C. Nearest airport: _____

- D. Chemical available: H_2SO_4 _____
 HNO_3 _____
 $NaOH$ _____

VII. Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PLANT BUILD WASTE TREATMENT TOBACCO PROCESSING



Justification for Toxic compound selection

An analysis of each production process was undertaken to evaluate those pollutants which could potentially be present in the process effluent. Emphasis was placed on pollutants potentially present due to production and/or subsequent wastewater treatment.

This analysis typically involved first a compilation of information from respective NPDES permit files. This information, yielding location, type or types of processes, general flow diagrams, etc., was then applied to the list of references^{sup} for each preliminary report. These additional references yielded information regarding reactants, products, byproducts, general unit operations employed and their parameters, plant specific information where known, experience with similar plants or industries, and finally, actual wastewater characterization data for each industry type.

Possible pollutant sources in the process wastewaters included water as a product of combustion or other process reaction, direct contact cooling water, product wash water, reactor washout wastes, condenser and scrubber water which has contacted either products or reactants, non-contact cooling water which may be contaminated due to process flange leaks, etc and finally, pollutants which may be produced as a result of the wastewater treatment system unit operations.

The analysis protocol for Phase I calls for automatically monitoring NPDES parameters, phenol, cyanide, inorganic ions and 76 elemental compounds. Therefore, organic compounds are the major output of this exercise.

No formal consideration was given to possible background contamination; e.g. plant intake waters, as the program is concerned with the contribution emanating from a particular production point source.

The list of organic compounds finally generated was evaluated to determine the toxicity of its members.

As stated in the project work plan, those compounds suspected to be particularly toxic are to be semi-quantified, whenever possible, with the remainder of the list scanned for via mass spectrometry.

The toxicity evaluation parameters were as follows:

Any lethality rating < 500 mg/kg	→	semi-quantify
Any identified carcinogenicity	→	semi-quantify
Any identified mutagenicity	→	semi-quantify
Any identified teratogenicity	→	semi-quantify
Any known toxic decomposition products	→	semi-quantify
None of the above	→	qualify via M. S.

Plant B111D is engaged in both tobacco processing and cigarette paper manufacture. The compounds selected were based on solvents and/or extractants used in tobacco preparation. Other compounds selected were done so because of the nature of the paper making process. Experimental data from sampling at analogous industries was evaluated to determine those processes related compounds which might be present.

Suspected Pollutants B111D

Glycerol

2,4,6-Trichlorophenol *

Chloroform *

2,4-Dichlorophenol *

Trichlorofluoromethane

Pentachlorophenol *

Phenol *

Pyridine, 3-(1-methyl-2-pyrrolidinyl) *

* To be semi-quantified due to potential toxicity, carcinogenicity, mutagenicity or teratogenicity.

All sampling and testing methods for this plant are anticipated to be identical to those outlined in the project work plan, dated 26 November, 1979. Any deviations are noted herein.

References

1. Gerstle, R., and J. Richards. Industrial Process Profiles For Environmental Use. EPA-600/2-77-023d, U.S. Environmental Protection Agency, Cincinnati, OHIO, February 1977
2. Letkiewicz F. Chemicals Which Have Been Tested For Neurotoxic Effects. EPA-360/1-76-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1976. 1332 pp.
3. Markle, R. A., Fentiman, A. F., Steadman, T. R. and R. A. Mayer. An Assessment of the Treatment and Control of Wastes From the Manufacture and Use of Potentially Toxic and Hazardous Organic Chemicals. U.S. Environmental Protection Agency (Patelle Columbus Laboratories Contract Number 68-02-1323). Cincinnati, OHIO, June 1974. 290 pp.

4. Watkins, D.R. Review of Industrial Organic Chemicals Processes for Potentially Toxic Materials. Contract Number 68-03-2579. Environmental Protection Agency, Cincinnati, Ohio, August, 1978.
5. STANDARD INDUSTRIAL CLASSIFICATION MANUAL, Executive Office of the President / BUREAU OF THE Budget, 1976. pp 615.
6. Dorigan, J., Fuller, B. and R. Duffy. Scoring of Organic Air Pollutants Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals. Contract Number 68-02-1995, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1976. 331 pp.
7. Fairchild, E. J. Registry of Toxic Effects of Chemical Substances. Contract Number 210-75-0034, U.S. Department of Health, Education and Welfare. 1977 edition.
8. U.S. EPA Wastewater Treatability Manual, draft Monsanto Research Corp. 1979.
9. State and Region NPDES permit files.

PRESURVEY DATA SHEETS

I. NAME OF COMPANY B113D DATE OF SUMMARY _____

ADDRESS _____ PHONE _____

NAME OF CONTACTS Information available

MRC PERSONNEL David Dunn PHONE (713) 268-3411

David Vanek PHONE _____

EPA PERSONNEL _____ PHONE _____

_____ PHONE _____

STATE PERSONNEL _____ PHONE _____

_____ PHONE _____

INDUSTRY TYPE nylon manufacturing SIC 2821 and 2824

PORTION OF PROCESS TO BE SAMPLED outfall 002 (final waste treatment outfall)

II. PROCESS DESCRIPTION Manufactures synthetic resins, plastics materials, and nonvulcanizable elastomers and synthetic organic fibers in the form of monofilament, yarn, staple, or tow (suitable) for further manufacture. Manufactures nylon (66) and four other products.

II. Con't.

Raw materials and amounts _____

Fuels oil and coal - no wet scrubbers

Products and amounts _____

Operating Cycle:

Check: Batch _____ Continuous _____ Cyclic _____

Timing of batch or cycle _____

Best time to sample _____

Length of Operating day 24hr

Length of operating week 7 day

Scheduled shutdowns none

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: neutralization,
oxidation, and polishing

Chemicals added and amounts neutralization (lime)

Handles rainfall runoff? yes

Includes sanitary waste, flow NPDES permit application

Source of plant intake water River

Hydraulic retention time: Thru plant _____

Thru treatment
unit operations over all 3-5 days - lagoon

2 days

Recent treatment plant performance excellent

III. Con't.

NPDES permit parameters and limits outfall 001 temp. (40°C max),
PH (6.0-9.0); outfall 002 [BOD5 (273 kg/day avg.) COD (7184
kg/day avg.), TSS (701 kg/day avg.), Nickel (27.3 kg/day avg.), Zn (9.5 kg/day avg.)
 Final effluent flow rate N/A HNPA 14 kg/day
 List of potential pollutants see attached list

Recent analyses available? _____

Sampling point description see attachment
@ outfall 002.

Use automatic sampler? yes

Electricity available yes

Extension cord and type of outlet? see escort

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses	✓	✓	Dust masks		
Goggles			Vapor masks		
Side shields	✓		Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes	✓	✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions restricted to designated areas
2. Vehicle traffic rules 15 mph - passing of moving vehicles & equipment prohibited - safety belt worn at all times - horn blown before picking up
3. Possible set-up/clean-up facilities? environmental control station (with permission)
4. Evacuation procedures direction given by escort
5. Alarms Plant whistle 8:00 AM and 4:00 PM, 9:30 AM
6. Hospital location nearest information available
7. Hospital Phone information available
- Emergency Numbers for escort

V. Plant Entry

- A. Plant Requirements authorized Minto plant - escort - NO cameras - truck pass - U.S. citizens (with permission) aliens
- Special time constraints: permitted by escort

B. MRC Agreement NO

C. Potential Problems

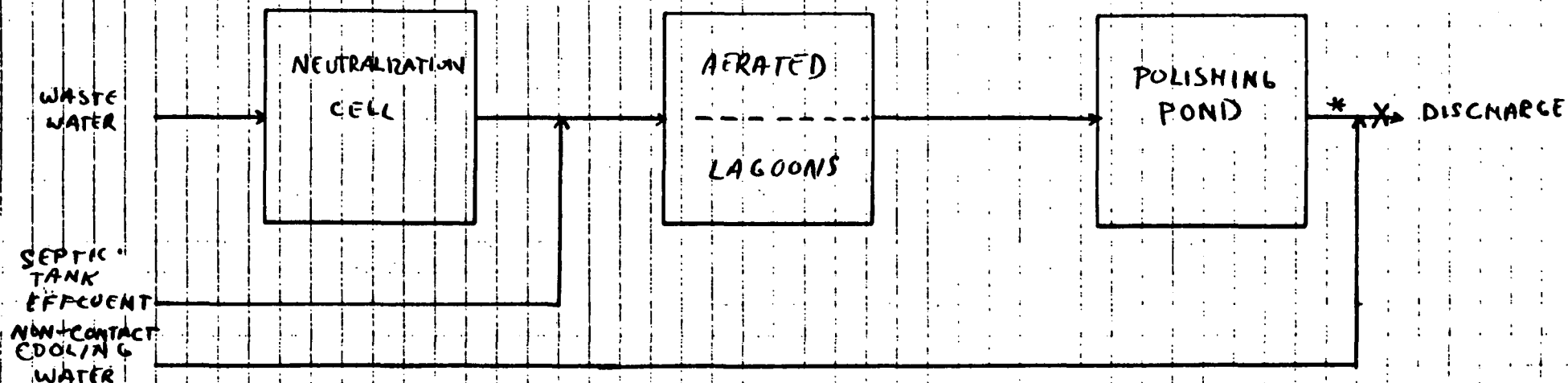
VI. SAMPLING HANDLING

- A. Ice availability See Local Grocery store
- B. Sample splitting requested Yes
Describe inorganic (plastic), organic (glass)
and, grabs (MRC will provide vials for grabs)
- C. Nearest airport: information available
- D. Chemical available: H_2SO_4 _____
 HNO_3 _____
 $NaOH$ _____

VII Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PLANT B113 D WASTE TREATMENT
NYLON MANUFACTURING



* Sample Collection Point
(upstream from the non-
contact cooling water)
@ outfall 002

Justification for Toxic compound selection

An analysis of each production process was undertaken to evaluate those pollutants which could potentially be present in the process effluent. Emphasis was placed on pollutants potentially present due to production and/or subsequent wastewater treatment.

This analysis typically involved first a compilation of information from respective NPDES permit files. This information, yielding location, type or types of processes, general flow diagrams, etc., was then applied to the list of references^{guy} for each preliminary report. These additional references yielded information regarding reactants, products, byproducts, general unit operations employed and their parameters, plant specific information where known, experience with similar plants or industries, and finally, actual wastewater characterization data for each industry type.

Possible pollutant sources in the process wastewaters included water as a product of combustion or other process reaction, direct contact cooling water, product wash water, reactor washout wastes, condenser and scrubber water which has contacted either products or reactants, non-contact cooling water which may be contaminated due to process flange leaks, etc and finally, pollutants which may be produced as a result of the wastewater treatment system unit operations.

The analysis protocol for Phase I calls for automatically monitoring NPDES parameters, phenol, cyanide, inorganic ions and 76 elemental compounds. Therefore, organic compounds are the major output of this exercise.

No formal consideration was given to possible background contamination; e.g. plant intake waters, as the program is concerned with the contribution emanating from a particular production point source.

The list of organic compounds finally generated was evaluated to determine the toxicity of its members.

As stated in the project work plan, those compounds suspected to be particularly toxic are to be semi-quantified, whenever possible, with the remainder of the list scanned for via mass spectrometry.

The toxicity evaluation parameters were as follows:

Any lethality rating $< 500 \text{ mg/kg}$	→ semi-quantify
Any identified carcinogenicity	→ semi-quantify
Any identified mutagenicity	→ semi-quantify
Any identified teratogenicity	→ semi-quantify
Any known toxic decomposition products	→ semi-quantify
None of the above	→ qualify via M. S.

Plant B113D is a synthetic resin facility. Major processes include various types of Nylon®. The compounds selected are feedstocks, products, byproducts and solvents. Data from this industry was reviewed to determine those compounds which could be attributed to the actual manufacturing process.

Suspected Pollutants

Cyclohexane*

Cyclohexanol

Cyclohexanone

Adipic acid

Hexamethylenediamine

Acetic acid*

Toluene*

Tetrahydrofuran*

Dimethylamine

Caprolactam

Ethylene diamine*

Hydrazine

Piperazine

Teraphthalic acid

* hexamethylphosphoramide

* To be semi-quantified due to potential toxicity, carcinogenicity, mutagenicity or teratogenicity.

All sampling and testing methods for this plant are anticipated to be identical to those outlined in the prepat. work plan, dated 26 November, 1979. Any deviations are noted herein.

References:

1. Gerstle, R., and J. Richards. "Industrial Process Profiles for Environmental Use." EPA-600/3-79-123a, U.S. Environmental Protection Agency, Cincinnati, Ohio, February 1979.
2. Lathewicz, E. "Chemicals Which Have Been Tested for Neurotoxic Effects." EPA-600/3-76-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1976. 1332 pp.
3. Markle, R. E., Fentiman, R. F., Steadman, J. R. and R. H. Mayer. "An Assessment of the Treatment and Control of Wastes From the Manufacture and Use of Potentially Toxic and Hazardous Organic Compounds." U.S. Environmental Protection Agency, Office of Research and Development Contract Number 68-02-1323. Cincinnati, Ohio, June 1974. 290 pp.

4. Watkins, D.R. Review of Industrial Organic Chemicals Processes for Potentially Toxic Materials. Contract Number 68-03-2579. Environmental Protection Agency, Cincinnati, Ohio, August, 1978.
5. STANDARD INDUSTRIAL CLASSIFICATION MANUAL, Executive Office of the President / BUREAU of the Budget, 1976. pp 665.
6. Dorigan, J., Fuller, B. and R. Duffy. Scoring of Organic Air Pollutants Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals. Contract Number 68-02-1495, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1976. 331 pp.
7. Fairchild, E. J. Registry of Toxic Effects of Chemical Substances. Contract Number 210-75-0034, U.S. Department of Health, Education and Welfare. 1977 edition.
8. U.S. EPA Wastewater Treatability Manual, draft Monsanto Research Corp. 1979,
9. State and Region NPDES permit files.

PRESURVEY DATA SHEETS

I. NAME OF COMPANY B124D DATE OF SUMMARY _____
ADDRESS _____ PHONE _____

NAME OF CONTACTS Information available

MRC PERSONNEL David Dunn PHONE (513) 268-3411
David Vanek PHONE _____
EPA PERSONNEL _____ PHONE _____

PHONE _____
STATE PERSONNEL _____ PHONE _____

PHONE _____
INDUSTRY TYPE Tobacco Processing (SIC 2111)

PORTION OF PROCESS TO BE SAMPLED Outfall 001

II. PROCESS DESCRIPTION The manufacturing facility produces a reconstituted tobacco product from tobacco materials. The process is proprietary.

II. Con't.

Raw materials and amounts Tobacco materials - 115 MM lbs/yr.

Fuels Coal, Nos. 2 and 6 fuel oil

Products and amounts Reconstituted tobacco material - 95 MM lbs./yr.

Operating Cycle:

Check: Batch _____ Continuous x Cyclic _____

Timing of batch or cycle _____

Best time to sample Anytime other than scheduled shutdowns

Length of Operating day 24 hours

Length of operating week 7 days

Scheduled shutdowns not available at this time

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: Extended aeration, activated

sludge, tertiary treatment system consisting of pretreatment (bar rack,
aerated grit chamber and coarse screen), primary treatment (three - 35'
diameter x 9' deep clarifiers and 300,000 gallon equalization basin),
secondary treatment (three - 2.5 MG aeration basins and four - 40' diameter
x 8' deep clarifiers), chlorination (two rectangular, baffled contact chambers),
filtration (three multi-media gravity filters with 1.5 MGD capacity and three
dual media pressure filters with 1.0 MGD capacity) and sludge thickening and
dewatering (two - 35' diameter x 8' deep clarifiers, two vacuum coil filters with
belt filter press).
Chemicals added and amounts Polymers and chlorine (vary with season and
operation)

Handles rainfall runoff? No

Includes sanitary waste, flow No

Source of plant intake water James River Water 1-1-1

Hydraulic retention time: Thru plant 5.6 days (134.8 hours)

Thru treatment
unit operations Pretreatment - 0.2 hours, Primary - 3.4 hours

Secondary - 130.2 hours. Chlorination - 0.8 hours and Filtration - 0.2 hours

Recent treatment plant performance Excellent

III. Con't.

NPDES permit parameters and limits SS - 300 ppd avg., 600 ppd max;

BOD₅ - 400 ppd avg., 800 ppd max., pH - 6.0 - 8.5; color - 400 APHA units

(24 hr. composite sample); and chlorine residual - 1.5 - 2.5 ppm with 12 (over)

Final effluent flow rate Nominal 1,000 gpm

List of potential pollutants See attached sheet

Recent analyses available? NPDES Permit Reports (Monthly)

Sampling point description Side stream to sample*trough located in

pressure filter building. Trough similar to small sink 6"x6"x6"

with adjustable flow. Mounted ~ 4 ft high on wall. Sampler Section

line weights probably not necessary. Sample directly out of Trough.

Use automatic sampler? Yes

Electricity available Yes

Extension cord and type of outlet? Yes

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses	X	✓	Dust masks		
Goggles			Vapor masks		
Side shields	X		Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes	X	✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid	X	✓

B. SAMPLE SITE

1. Smoking restrictions None
2. Vehicle traffic rules Speed limit within facility is 15 MPH and parking location will be designated upon arrival, truck pass needed.
3. Possible set-up/clean-up facilities? Yes
4. Evacuation procedures None
5. Alarms _____
6. Hospital location Information Available
7. Hospital Phone Information Available
- Emergency Numbers _____

V. Plant Entry

- A. Plant Requirements Visitors must sign in and out of facility at Receptionist Desk or Security Gatehouse where they will receive facility pass. See Receptionist upon arrival.
- Special time constraints: Receptionist Desk - 8:30 a.m. to 5:00 p.m., Security Gatehouse - 24 hours/day

B. MRC Agreement _____

C. Potential Problems _____

VI. SAMPLING HANDLING

A. Ice availability See local store

B. Sample splitting requested yes

Describe 1 gal of each + repeat grabs (6)
MRC will provide vials for grab samples.

C. Nearest airport: _____

D. Chemical available: H_2SO_4 _____

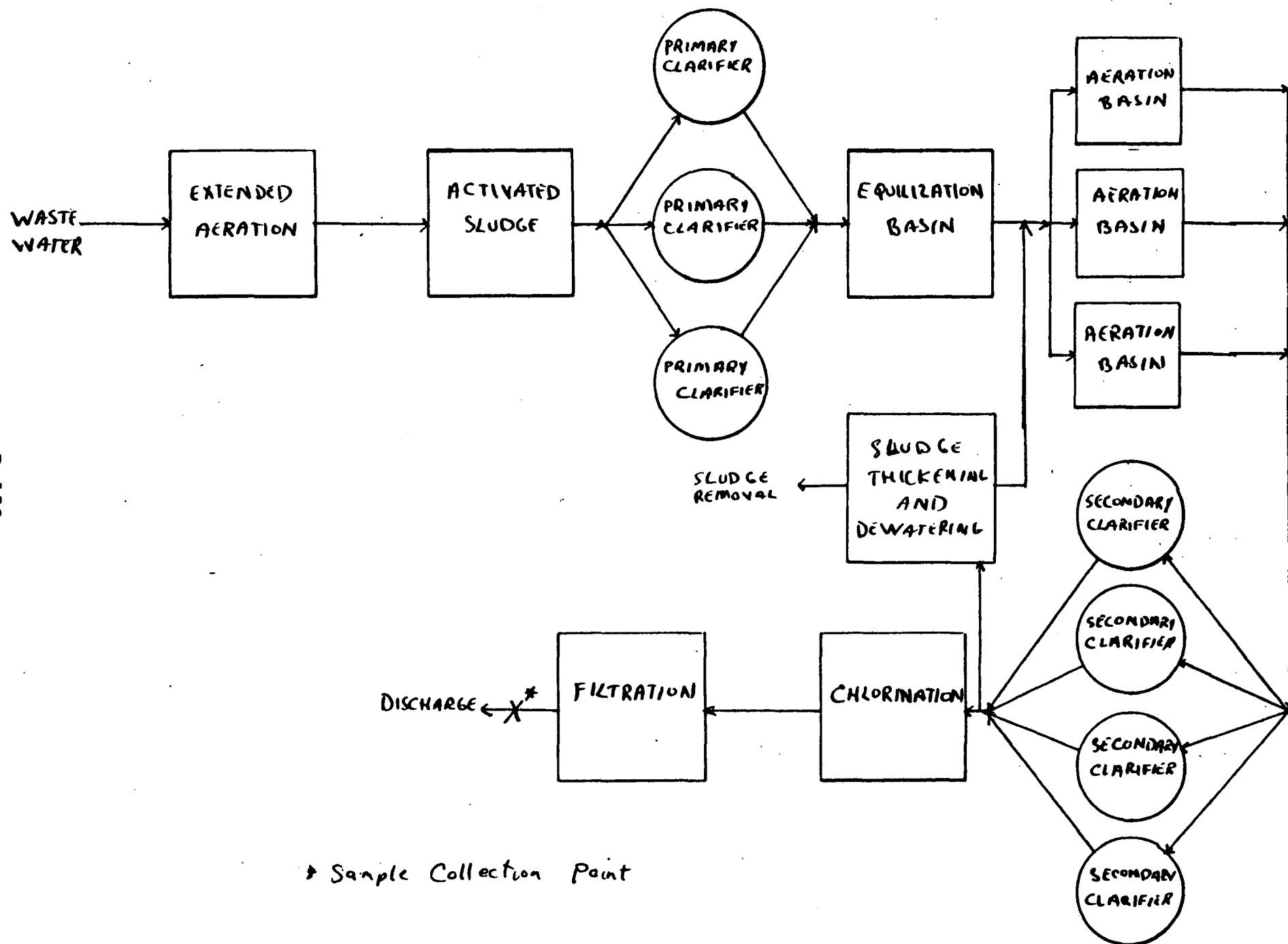
HNO_3 _____

$NaOH$ _____

VII. Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PLANT BIOD WASTE TREATMENT
TOBACCO PROCESSING



Justification for Toxic compound selection

An analysis of each production process was undertaken to evaluate those pollutants which could potentially be present in the process effluent. Emphasis was placed on pollutants potentially present due to production and/or subsequent wastewater treatment.

This analysis typically involved first a compilation of information from respective NPDES permit files. This information, yielding location, type or types of processes, general flow diagrams, etc., was then applied to the list of references^{for} for each presurvey report. These additional references yielded information regarding reactants, products, byproducts, general unit operations employed and their parameters, plant specific information where known, experience with similar plants or industries, and finally, actual wastewater characterization data for each industry type.

Possible pollutant sources in the process wastewaters included water as a product of combustion or other process reaction, direct contact cooling water, product wash water, reactor washout wastes, condenser and scrubber water which has contacted either products or reactants, non-contact cooling water which may be contaminated due to process flange leaks, etc and finally, pollutants which may be produced as a result of the wastewater treatment system unit operations.

The analysis protocol for Phase I calls for automatically monitoring NPDES parameters, phenol, cyanide, inorganic ions and 76 elemental compounds. Therefore, organic compounds are the major output of this exercise.

No formal consideration was given to possible background contamination, e.g. plant intake waters, as the program is concerned with the contribution emanating from a particular production point source.

Plant B124D is engaged in tobacco product processing. Compounds collected are solvents or major process inputs in the raw material.

The list of organic compounds finally generated was evaluated to determine the toxicity of its members.

As stated in the project work plan, those compounds suspected to be particularly toxic are to be semi-quantified, whenever possible, with the remainder of the list scanned for via mass spectrometry.

The toxicity evaluation parameters were as follows:

Any lethality rating $< 500 \text{ mg/kg}$	→ semi-quantify
Any identified carcinogenicity	→ semi-quantify
Any identified mutagenicity	→ semi-quantify
Any identified teratogenicity	→ semi-quantify
Any known toxic decomposition products	→ semi-quantify
None of the above	→ qualify via M. S.

Suspected Pollutants B124D

ethanol*

glycerol

pyridine, 3-(1-methyl-2-pyrrolidinyl)*

*To be semi-quantified due to potential toxicity, carcinogenicity, mutagenicity or teratogenicity

All sampling and testing methods for this plant are anticipated to be identical to those outlined in the project work plan, dated 26 November, 1979. Any deviations are noted herein.

References

1. Gerstle, R., and J. Richards. Industrial Process Profiles For Environmental Use. EPA-600/2-77-023d, U.S. Environmental Protection Agency, Cincinnati, OHIO, February 1977.
2. Letkiewicz F. Chemicals Which Have Been Tested For Neurotoxic Effects. EPA-360/1-76-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1976. 1332 pp.
3. Markle, R. A., Fentiman, A. F., Steadman, T. R. and R. A. Mayer. An Assessment of the Treatment and Control of Wastes From the Manufacture and Use of Potentially Toxic and Hazardous Organic Chemicals. U.S. Environmental Protection Agency (Rutledge Columbus Laboratories Contract Number 68-02-1323). Cincinnati, OHIO, June 1974. 290 pp.

4. Watkins, D.R. Review of Industrial Organic Chemicals Processes for Potentially Toxic Materials. Contract Number 68-03-2579. Environmental Protection Agency, Cincinnati, Ohio, August, 1978.
5. STANDARD INDUSTRIAL CLASSIFICATION MANUAL, Executive Office of the President / BUREAU of the Budget, 1976. pp 665.
6. Dorigan, J., Fuller, B. and R. Duffy. Scoring of Organic Air Pollutants Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals. Contract Number 68-02-1995, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1976. 331 pp.
7. Fairchild, E. J. Registry of Toxic Effects of Chemical Substances. Contract Number 210-75-0034, U.S. Department of Health, Education and Welfare. 1977 edition.
8. U.S. EPA Wastewater Treatability Manual, draft Monsanto Research Corp. 1979.
9. State and Region NPDES permit files.

II. Con't.

Raw materials and amounts _____

Fuels COAL AND OIL FOR ELECTRICAL PRODUCTION

Products and amounts _____

Operating Cycle:

Check: Batch ☒ Continuous ☒ Cyclic _____

Timing of batch or cycle METALS TREATMENT BASIN IS BATCH
REFER TO FLOW DIAGRAM PERIODIC Ref

Best time to sample ANYTIME

Length of Operating day 24 hrs

Length of operating week 7 days

Scheduled shutdowns NONE

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: _____

REFER TO DIAGRAM
Stabilization Pond

Chemicals added and amounts Lime to control pH

Handles rainfall runoff? NO

Includes sanitary waste, flow NO

Source of plant intake water JAMES RIVER

Hydraulic retention time: Thru plant NA
Thru treatment
unit operations _____

Recent treatment plant performance Refer to Summaries

III. Con't.

NPDES permit parameters and limits Free Chlorine = 2mg/l (Daily Avg) 5mg/l (Daily Max)
Temp. = Heat rejected to the waterway shall not exceed a max. of 11.3×10^6 BTU/HR.

Final effluent flow rate N/A

List of potential pollutants _____

Copper, Iron, Arsenic, Oil + Grease
Cadmium, Chromium Nickel

Recent analyses available? Refer to summaries

Sampling point description WEIR — outfall from the lagoon

Use automatic sampler? Grab sample

Electricity available No

Extension cord and type of outlet? _____

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions _____
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? YES
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location MCV, Richmond
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

A. Plant Requirements I.D. CARD

Special time constraints: 0800 to 1700

B. MRC Agreement _____

C. Potential Problems _____

VI. SAMPLING HANDLING

A. Ice availability _____

B. Sample splitting requested _____

Describe _____

C. Nearest airport: Byrd or Chesterfield County

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VIL Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

CALL

PRESURVEY DATA SHEETS

I. NAME OF COMPANY C153D DATE OF SUMMARY 5/12/81

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

_____ PHONE _____

EPA PERSONNEL _____ PHONE _____

_____ PHONE _____

STATE PERSONNEL _____ PHONE _____

_____ PHONE _____

INDUSTRY TYPE Fertilizer Production (MIXED GRANULAR)

PORTION OF PROCESS TO BE SAMPLED Outfall 001

II. PROCESS DESCRIPTION PHOSPHATE PULVERIZATION,
ACID TREATMENT, ACID RECLAMATION
BLEND FERTILIZER

II. Con't. ^{TRIPLE SUPER} ~~GRANULAR~~ ^{MURIATE OF POTASH} ~~DIAMMONIUM~~ ^{PHOSPHATE} ~~Limestone~~
^{TRACE ELEMENTS} ~~Nitrogen~~ ^{Ammonium} ~~Nitrate~~ ^{Sulphate of NH₄}
^{Phosphoric Acid} ~~Molten Sulphur~~ ^{Spart Sulphate} ~~Phosphate Rock~~
Raw materials and amounts _____
Fuels _____
Products and amounts SUPER PHOSPHATE
FLUORIC ACID

Operating Cycle:

Check: Batch _____ DISCHARGE
Continuous ✓ Cyclic _____

Timing of batch or cycle _____

Best time to sample 0800 to 1700

Length of Operating day 0800 to 1700

Length of operating week 5 days

Scheduled shutdowns NO

Other PROCESS may not be continuous

III. WASTEWATER TREATMENT PLANT DESCRIPTION: _____

COOLING WATER + RUNOFF
DRAINAGE DITCH TO RIVER

Chemicals added and amounts NONE

Handles rainfall runoff? YES

Includes sanitary waste, flow NO

Source of plant intake water WELL + City of Chesapeake (MAJOR)

Hydraulic retention time: Thru plant NO RETENTION
Thru treatment
unit operations _____

Recent treatment plant performance _____

III. Con't.

NPDES permit parameters and limits Oil & Grease = 10 mg/l (DAILY AVG)
15 mg/l (DAILY MAX) Temp = 105°F (DAILY MAX) pH = 6.0 to 8.5 AT ALL TIMES

Final effluent flow rate N/A NO LIMIT

List of potential pollutants' ACID LEAKS (SULPHURIC)

Recent analyses available? Refer to Summaries

Sampling point description DISCHARGE POINT INTO
DITCH THAT EMPTIES INTO ELIZABETH RIVER

Use automatic sampler? Grab Sample

Electricity available YES

Extension cord and type of outlet? 100 ft. CORD

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions _____
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? _____
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location _____
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

A. Plant Requirements I.D CARD

Special time constraints: _____

B. MRC Agreement _____

C. Potential Problems NONE

VI. SAMPLING HANDLING

A. Ice availability _____

B. Sample splitting requested _____

Describe _____

C. Nearest airport: Worfolk International

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VII. Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY C154D DATE OF SUMMARY 5/12/81

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

_____ PHONE _____

EPA PERSONNEL _____ PHONE _____

_____ PHONE _____

STATE PERSONNEL _____ PHONE _____

_____ PHONE _____

INDUSTRY TYPE Fertilizer

PORTION OF PROCESS TO BE SAMPLED Outfall 001 Storm Water
Surface Drain + Cooling Waters

II. PROCESS DESCRIPTION MANUF. AMMONIATED FERTILIZER
COOLING SULPHURIC ACID WHEN CUTTING ACID

N/A TO SAMPLE TAKEN

II. Con't.

Raw materials and amounts

N/A

Fuels

Products and amounts

N/A

Operating Cycle:

Check: Batch



Continuous

Cyclic

Timing of batch or cycle

Best time to sample

0800 to 1700

Length of Operating day

0800 to

Length of operating week

5 DAYS

Scheduled shutdowns

NONE

Other

Intermittent Processing

III.

WASTEWATER TREATMENT PLANT DESCRIPTION:

NON-CONTACT

ACID COOLING (WATER TAKEN FROM ELIZABETH RIVER)

Chemicals added and amounts

N/A

Handles rainfall runoff?

YES

Includes sanitary waste, flow

N/A

Source of plant intake water

WELL

Hydraulic retention time:, Thru plant

CONTINUOUS

Thru treatment
unit operations

Recent treatment plant performance

Refer To summaries

III. Con't.

NPDES permit parameters and limits Temp. = 90°F (DAILY MAX.)
pH = 6.0 TO 8.5 At All times

Final effluent flow rate N/A

List of potential pollutants only TAKE pH

Recent analyses available? _____

Sampling point description _____

Use automatic sampler? GRAB SAMPLE

Electricity available YES

Extension cord and type of outlet? _____

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

<u>Item</u>	<u>Plant</u>	<u>MRC</u>	<u>Item</u>	<u>Plant</u>	<u>MRC</u>
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions _____
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? _____
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location Hampton Blvd. - Norfolk Gen.
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

- A. Plant Requirements I.D. CARD

Special time constraints: Intermittant Processing

- B. MRC Agreement _____

- C. Potential Problems NONE

VI. SAMPLING HANDLING

A. Ice availability _____

B. Sample splitting requested _____

Describe _____

C. Nearest airport: Norfolk International

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VII Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY C158D DATE OF SUMMARY 5/14/81
ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

PHONE _____

EPA PERSONNEL _____ PHONE _____

PHONE _____

STATE PERSONNEL _____ PHONE _____

PHONE _____

INDUSTRY TYPE (Municipal) Sewage Treatment

PORTION OF PROCESS TO BE SAMPLED Effluent outfall 001

II. PROCESS DESCRIPTION SECONDARY ACTIVATED SLUDGE ○

II. Con't.

Raw materials and amounts N/A

Fuels N/A

Products and amounts N/A

Operating Cycle:

Check: Batch _____ Continuous ✓ Cyclic _____

Timing of batch or cycle N/A

Best time to sample 0800 to 1700

Length of Operating day 24 hrs

Length of operating week 7 days

Scheduled shutdowns NONE

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION:

REFER to flow diagram SECONDARY-
ACTIVATED SLUDGE

Chemicals added and amounts LIME 8,000 lbs/day
3000 lbs/day = Chlorine Ferric Chloride 3000

Handles rainfall runoff? YES

Includes sanitary waste, flow YES

Source of plant intake water N/A

Hydraulic retention time: Thru plant 10-11 hours
Thru treatment
unit operations _____

Recent treatment plant performance _____

III. Con't.

NPDES permit parameters and limits BOD₅ = 1000 lbs/day (avg), 10.3 mg/l monthly avg
TSS = 1000 lbs/day avg, 10.3 mg/l monthly avg, pH = 6.0 to 9.0, fecal coli. = 200 monthly, 90 weekly

Final effluent flow rate 70 MGD

List of potential pollutants N/A 0

Recent analyses available? REFER TO SUMMARIES

Sampling point description Chlorine Contact Tank

Use automatic sampler? GRAB SAMPLE OF
110 GALLONS

Electricity available YES

Extension cord and type of outlet? 75ft.

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions n/a
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? YES
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location Medical College of VA.
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

A. Plant Requirements I.D. CARD

Special time constraints: 0800 to 1700

B. MRC Agreement _____

C. Potential Problems NONE

VI. SAMPLING HANDLING

A. Ice availability _____

B. Sample splitting requested _____

Describe _____

C. Nearest airport: Byrd _____

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VIL Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY C159D DATE OF SUMMARY 5/12/81

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

PHONE _____

EPA PERSONNEL _____ PHONE _____

PHONE _____

STATE PERSONNEL _____ PHONE _____

PHONE _____

INDUSTRY TYPE MEAT (PORK) PROCESSING
SLAUGHTER AND PACKAGING

PORTION OF PROCESS TO BE SAMPLED OUTGALL 001

II. PROCESS DESCRIPTION SLAUGHTER (4,000 to 5,000 HOGS) →
Chilling → CUTTING → PACKAGE VARIOUS MEATS

II. Con't.

Raw materials and amounts 4,500 HOGS SLAUGHTERED DAILY

Fuels _____

Products and amounts 4 1/2 MILLION POUNDS OF PORK PRODUCTS/WK.

Operating Cycle:

Check: Batch _____ Continuous ✓ Cyclic _____

Timing of batch or cycle _____

Best time to sample 0800 to 1700

Length of Operating day 0600 to 1800

Length of operating week 5 days

Scheduled shutdowns NONE

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION:

(Pre-treatment)
FOR GREASE AND SCUM → GRIT REMOVAL → EXTENDED
AERATION (3 PONDS) → CLARIFICATION → CHLORINATION
→ DISCHARGE.

Chemicals added and amounts Chlorine 1.5 to 2.5 ppm RESIDUAL

Handles rainfall runoff? YES 75% OF STORM DRAINS

Includes sanitary waste, flow NO

Source of plant intake water _____

Hydraulic retention time: Thru plant 2 1/2 DAYS TO 1 WEEK
Thru treatment
unit operations _____

Recent treatment plant performance Refer to Summaries

III. Con't.

NPDES permit parameters and limits _____

Final effluent flow rate _____

1.2 MGD

List of potential pollutants _____

NONE

Recent analyses available? _____

Sampling point description _____

Use automatic sampler? _____

GRAB

ONE 110 gal. COMPOSITE

Electricity available _____

YES

Extension cord and type of outlet? _____

110V

NO CORD NEEDED

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions _____
2. Vehicle traffic rules _____

3. Possible set-up/clean-up facilities? NONE
4. Evacuation procedures _____

5. Alarms _____
6. Hospital location _____
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

- A. Plant Requirements I.D. CARD

- Special time constraints: _____

- B. MRC Agreement _____

- C. Potential Problems NONE

VI. SAMPLING HANDLING

A. Ice availability _____

B. Sample splitting requested _____

Describe _____

C. Nearest airport: _____

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VII Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY C160D DATE OF SUMMARY 5/12/81

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL _____ PHONE _____

PHONE _____

EPA PERSONNEL _____ PHONE _____

PHONE _____

STATE PERSONNEL _____ PHONE _____

PHONE _____

INDUSTRY TYPE Fabricate rubber products AND mechanical rubber goods

PORTION OF PROCESS TO BE SAMPLED Outfall 001

II. PROCESS DESCRIPTION GASKET MANUFACTURE
GRIND RAW CORK → MIX WITH ^(VARIOUS) BINDERS → CUT GASKETS

II. Con't.

Raw materials and amounts

RAW CORK / POLYURETHANE / Synthetic Rubber

Fuels

Products and amounts

GASKETS AND AUTO SOUND DEADENING MATERIAL

Operating Cycle:

Check: Batch

Continuous

☒

Cyclic

Timing of batch or cycle

N/A

Best time to sample

0800 - 1700

Length of Operating day

24 HRS.

Length of operating week

5 days

Scheduled shutdowns

NONE

Other

III.

WASTEWATER TREATMENT PLANT DESCRIPTION:

Cooling tank and dilution prior to discharge.

Chemicals added and amounts

N/A

Handles rainfall runoff?

YES

Includes sanitary waste, flow

NONE

Source of plant intake water

WELLS

Hydraulic retention time: Thru plant

N/A

Thru treatment unit operations

Recent treatment plant performance

III. Con't.

NPDES permit parameters and limits TSS = 30mg/l (DAILY AVG),
Temp = 85°F (Daily MAX), pH = 6.0 to 8.5 at all times

Final effluent flow rate N/A

List of potential pollutants Oil AND GREASE

Recent analyses available? _____

Sampling point description _____

Use automatic sampler? GRAB Sample

Electricity available YES

Extension cord and type of outlet? 50

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

B. SAMPLE SITE

1. Smoking restrictions _____
2. Vehicle traffic rules MAY HAVE TO DRIVE
TRUCK INTO PLANT
3. Possible set-up/clean-up facilities? NO
4. Evacuation procedures _____
5. Alarms _____
6. Hospital location BANDRIDGE BLVD
7. Hospital Phone _____
- Emergency Numbers _____

V. Plant Entry

A. Plant Requirements I.D. CARD

Special time constraints: 0800-1700

B. MRC Agreement _____

C. Potential Problems _____

VI. SAMPLING HANDLING

A. Ice availability _____

B. Sample splitting requested _____

Describe _____

C. Nearest airport: Norfolk International

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VII Field Test Schedule

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PRESURVEY DATA SHEETS

I. NAME OF COMPANY B126 S DATE OF SUMMARY _____

ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL David Dunn and David Vande PHONE (513) 268-3411

PHONE _____

EPA PERSONNEL _____ PHONE _____

PHONE _____

STATE PERSONNEL _____ PHONE _____

PHONE _____

INDUSTRY TYPE Manufacture of Inorganic pigments by chemical precipitation and calcination (SIC 2816)

PORTION OF PROCESS TO BE SAMPLED Outfall 001 - colored pigment building

II. PROCESS DESCRIPTION Preparation of cadmium colors from cadmium, sulfur, and selenium plus additives and treating agents (Outfall 001). Also preparation of silica gel pigments from sodium silicate and sulfuric acid plus additives. (See diagram)

II. Con't.

Raw materials and amounts Cd, Barium Sulfide, Arsenic Sulfide, Se, H₂SO₄

Fuels Natural gas, #2 fuel oil

Products and amounts Pigments (proprietary data)

Operating Cycle:

Check: Batch ✓ Continuous _____ Cyclic _____

Timing of batch or cycle Various

Best time to sample low flow after 5:00 p.m. (Intermittent flow)

Length of Operating day 24 hours

Length of operating week 5 days

Scheduled shutdowns Last week of June, silica pigments on limited sched.

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: Metals are precipitated and filtered from waste water (See diagram)

Chemicals added and amounts Soda ash (varies), FeS (trace)

Handles rainfall runoff? No

Includes sanitary waste, flow No

Source of plant intake water City water

Hydraulic retention time: Thru plant _____

Thru treatment

unit operations Continuous process

Recent treatment plant performance Excellent

III. Con't.

NPDES permit parameters and limits NH₃ (9#/day), Cd (0.022#/day)

Final effluent flow rate _____

List of potential pollutants see attached sheet

Recent analyses available? No

Sampling point description 2' x 2' pump with 6'-8" water depth

Use automatic sampler? yes

Electricity available yes (115 V)

Extension cord and type of outlet? 2-prong plus ground for 115V service available

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses	✓*	✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes	✓*	✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid	✓	✓

* not required outside

B. SAMPLE SITE

1. Smoking restrictions No smoking in colors plant

2. Vehicle traffic rules 10 m.p.h.

3. Possible set-up/clean-up facilities? Lunch room

4. Evacuation procedures Copy will be provided

5. Alarms Voice intercom

6. Hospital location Information available

7. Hospital Phone _____

Emergency Numbers _____

V. Plant Entry

A. Plant Requirements Stop at gate. No pass needed for truck

Special time constraints: Plant superintendent will alert guard for work after 4:30 p.m.

B. MRC Agreement May be necessary

C. Potential Problems None

VI. SAMPLING HANDLING

A. Ice availability Local stores

B. Sample splitting requested yes

Describe Some of each especially metals not if 55 gal
sample but possibly grab

C. Nearest airport: Information available

D. Chemical available: H_2SO_4 _____

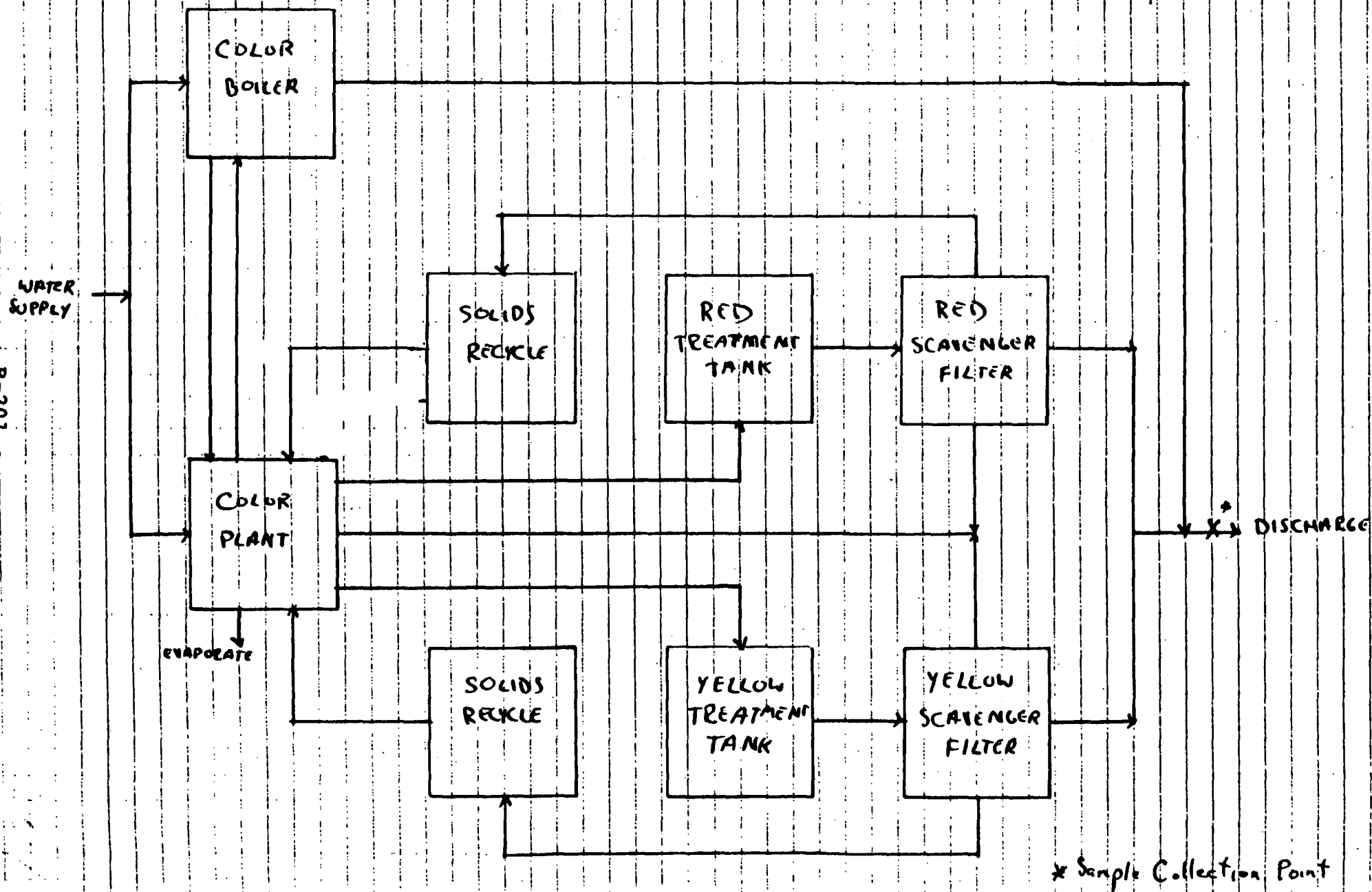
HNO_3 _____

$NaOH$ _____

VII. Field Test Schedule *Information available*

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PLANT B1265 WATER (SU) AND WASTE TREATMENT
INORGANIC PIGMENTS PRODUCTION



Justification for Toxic compound selection

An analysis of each production process was undertaken to evaluate those pollutants which could potentially be present in the process effluent. Emphasis was placed on pollutants potentially present due to production and/or subsequent wastewater treatment.

This analysis typically involved first a compilation of information from respective NPDES permit files. This information, yielding location, type or types of processes, general flow diagrams, etc., was then applied to the list of references for each preliminary report. These additional references yielded information regarding reactants, products, byproducts, general unit operations employed and their parameters, plant specific information where known, experience with similar plants or industries, and finally, actual wastewater characterization data for each industry type.

Possible pollutant sources in the process wastewaters included water as a product of combustion or other process reaction, direct contact cooling water, product wash water, reactor washout wastes, condenser and scrubber water which has contacted either products or reactants, non-contact cooling water which may be contaminated due to process flange leaks, etc and finally, pollutants which may be produced as a result of the wastewater treatment system unit operations.

The analysis protocol for Phase I calls for automatically monitoring NPDES parameters, phenol, cyanide, inorganic ions and 76 elemental compounds. Therefore, organic compounds are the major output of this exercise.

No formal consideration was given to possible background contamination; eg. plant intake waters, as the program is concerned with the contribution emanating from a particular production point source.

The list of organic compounds finally generated was evaluated to determine the toxicity of its members.

As stated in the project work plan, those compounds suspected to be particularly toxic are to be semi-quantified, whenever possible, with the remainder of the list scanned for via mass spectrometry.

The toxicity evaluation parameters were as follows:

Any lethality rating $< 500 \text{ mg/kg}$	→	semi-quantify
Any identified carcinogenicity	→	semi-quantify
Any identified mutagenicity	→	semi-quantify
Any identified teratogenicity	→	semi-quantify
Any known toxic decomposition products	→	semi-quantify
None of the above	→	qualify via M. S.

Plant B1265 is an inorganic pigments production facility. Previous samplings of facilities of this nature have indicated the presence of phenol in low levels. At present, this is the only organic to be specifically scanned for.

B126 S

SUSPECTED POLLUTANTS

Phenol *

* To be semi-quantified due to potential toxicity, carcinogenicity, mutagenicity or teratogenicity.

All sampling and testing methods for the plant are anticipated to be identical to those outlined in the project work plan, dated 26 November, 1979. Any deviations are noted herein.

References

1. Gerstle, R., and J. Richards. Industrial Process Profiles For Environmental Use. EPA-600/2-77-023d, U.S. Environmental Protection Agency, Cincinnati, OHIO, February 1977
2. Letkiewicz F. Chemicals Which Have Been Tested For Neurotoxic Effects. EPA-560/1-76-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1976. 1332 pp.
3. Markle, R.A., Fentiman, A.F., Steadman, T.R. and R.A. Mayer. An Assessment of the Treatment and Control of Wastes From the Manufacture and Use of Potentially Toxic and Hazardous Organic Chemicals. U.S. Environmental Protection Agency (Zettelle Columbus Laboratories Contract Number 68-02-1323). Cincinnati, OHIO, June 1974. 290 pp.

4. Watkins, D.R. Review of Industrial Organic Chemicals Processes for Potentially Toxic Materials. Contract Number 68-03-2579. Environmental Protection Agency, Cincinnati, Ohio, August, 1978.
5. STANDARD INDUSTRIAL CLASSIFICATION MANUAL, Executive Office of the President / BUREAU of the Budget, 1976. pp 615.
6. Dorigan, J., Fuller, B. and R. Duffy. Scoring of Organic Air Pollutants Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals. Contract Number 68-02-1495, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1976. 331 pp.
7. Fairchild, E. J. Registry of Toxic Effects of Chemical Substances. Contract Number 210-75-0034, U.S. Department of Health, Education and Welfare. 1977 edition.
8. Merck and Co., The Merck Index 9th Edition, 1976.

7. Barret, William J., et al, Waterborne Wastes of the Paint and Inorganic Pigments Industries, National Environmental Research Center Office of Research and Development U.S. Environmental Protection Agency, Cincinnati, OH 45268
10. Datagraphics Inc., Inorganic Chemicals Industry Profile (Updated), Environmental Protection Agency, July, 1971.

PRESURVEY DATA SHEETS

I. NAME OF COMPANY B/435 DATE OF SUMMARY _____
ADDRESS _____ PHONE _____

NAME OF CONTACTS _____

MRC PERSONNEL Stephen Victor and Don Mahone PHONE _____

EPA PERSONNEL _____ PHONE _____

STATE PERSONNEL _____ PHONE _____

INDUSTRY TYPE TiO₂ manufacturing (82816)

PORTION OF PROCESS TO BE SAMPLED Outfall CO₂

II. PROCESS DESCRIPTION Manufacture of Titanium dioxide pigments using chloride and sulfate hydrolysis precipitation manufacturing processes (see diagram)

II. ^{CONFIDENTIAL} COMPANY CONFIDENTIAL

Ti (100 TPD), coke, CaCO₃ (5-10 TPD)

COMPANY CONFIDENTIAL

^{C.I. Process} SO₄ Process

Raw materials and amounts Ti, Al (250 TPD), H₂SO₄ (400 TPD), CaCO₃ for vent.

Fuels _____

Products and amounts Li₂O₂ (45000 TPD), SO₄, 30000 TPD Cl

COMPANY CONFIDENTIAL

Operating Cycle:

Check: Batch Outlets Continuous Cl Cyclic _____

Timing of batch or cycle Highly varied

Best time to sample Anytime

Length of Operating day 24 hours

Length of operating week 7 days

Scheduled shutdowns Cl process may or may not be down

Other _____

III. WASTEWATER TREATMENT PLANT DESCRIPTION: Sulfuric acid is neutralized with calcium carbonate and the resulting calcium sulfate is removed by filtration. Iron is removed as ferric hydroxide by clarification and filtration. Hydrochloric acid is neutralized with alkali and suspended solids are settled by lagooning (see diagram)

Chemicals added and amounts CaCO₃, NaOH/NaClO₂, surfactants and coagulants

Handles rainfall runoff? Yes

Includes sanitary waste, flow Yes, for 650 people

Source of plant intake water city water (5.5 MGD)

Hydraulic retention time: Thru plant N.A.

Thru treatment unit operations Cl plant approx. 2-3 hours

SO₄ plant approx 2 days

Recent treatment plant performance Normal

III. Con't.

NPDES permit parameters and limits TSS (4320 #/day), pH (6.0-9.0)
Fe (1212 #/day)

Final effluent flow rate 55 MGD

List of potential pollutants See attached list

Recent analyses available? Quarterly DMRs

Sampling point description Take two composite and two
grab stb. will need six samples at plant. Do flow
proportioned - PWAN plant from SW process, chloride process

Use automatic sampler? yes

Electricity available yes

Extension cord and type of outlet? 3-prong, 10ft. (bring both type
of adapters)

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses		✓	Dust masks		
Goggles			Vapor masks*		✓
Side shields		✓	Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid		✓

* on person

B. SAMPLE SITE

1. Smoking restrictions None
2. Vehicle traffic rules Normal traffic rules - no vehicles past isolation
3. Possible set-up/clean-up facilities? No
4. Evacuation procedures None
5. Alarms Series of whistles from the vehicle CI failure - may need made
6. Hospital location Information available
7. Hospital Phone _____
- Emergency Numbers X272 or 247 -

V. Plant Entry

- A. Plant Requirements Come to personnel office and ask for appropriate personnel. Must have an escort at all times.

Special time constraints: Night entry may be a problem. Check later.

- B. MRC Agreement Security agreement

- C. Potential Problems None

VI. SAMPLING HANDLING

A. Ice availability Local stores

B. Sample splitting requested Yes

Describe No volatiles, NPDES parameters

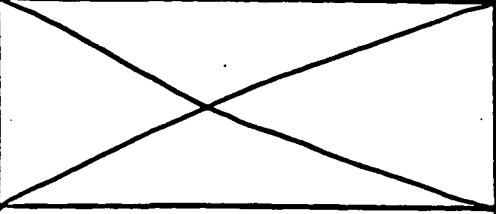
C. Nearest airport: Information available

D. Chemical available: H_2SO_4 _____

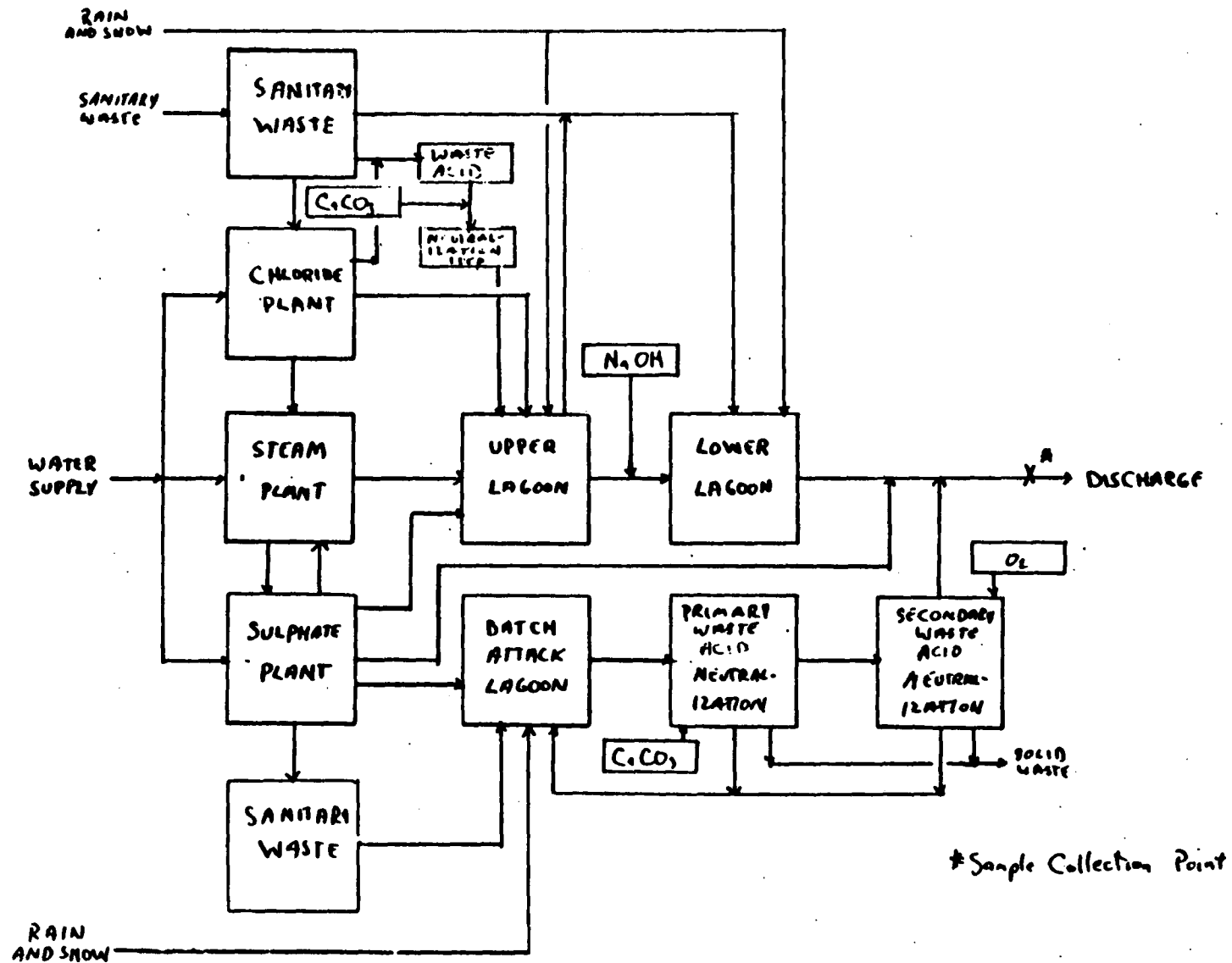
HNO_3 _____

$NaOH$ _____

VIL Field Test Schedule *Information available*

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

PLANT B1435 WAS TREATMENT AND WATER FLOW
T.O₂ PRODUCTION



Justification for Toxic compound selection

An analysis of each production process was undertaken to evaluate those pollutants which could potentially be present in the process effluent. Emphasis was placed on pollutants potentially present due to production and/or subsequent wastewater treatment.

This analysis typically involved first a compilation of information from respective NPDES permit files. This information, yielding location, type or types of processes, general flow diagrams, etc., was then applied to the list of references for each presurvey report. These additional references yielded information regarding reactants, products, byproducts, general unit operations employed and their parameters, plant specific information where known, experience with similar plants or industries, and finally, actual wastewater characterization data for each industry type.

Possible pollutant sources in the process wastewaters included water as a product of combustion or other process reaction, direct contact cooling water, product wash water, reactor washout wastes, condenser and scrubber water which has contacted either product or reactants, non-contact cooling water which may be contaminated due to process flange leaks, etc and finally, pollutants which may be produced as a result of the wastewater treatment system unit operations.

The analysis protocol for Phase I calls for automatically monitoring NPDES parameters, phenol, cyanide, inorganic ions and 76 elemental compounds. Therefore, organic compounds are the major output of this exercise.

No formal consideration was given to possible background contamination, e.g. plant intake waters, as the program is concerned with the contribution emanating from a particular production point source.

The list of organic compounds finally generated was evaluated to determine the toxicity of its members.

As stated in the project work plan, those compounds suspected to be particularly toxic are to be semi-quantified, whenever possible, with the remainder of the list scanned for via mass spectrometry.

The toxicity evaluation parameters were as follows:

Any lethality rating < 500 mg/kg	→ semi-quantify
Any identified carcinogenicity	→ semi-quantify
Any identified mutagenicity	→ semi-quantify
Any identified teratogenicity	→ semi-quantify
Any known toxic decomposition products	→ semi-quantify
None of the above	→ qualify via M. S.

Plant B1435 is engaged in inorganic pigment manufacture. Although no organics are attributable directly to the process, plant sanitary wastes and their chlorination are a suspected source for those compounds listed.

B143 S
SUSPECTED POLLUTANTS

Benzene *

Phenol *

Pentachlorophenol *

* To be semi-quantified due to potential toxicity, carcinogenicity, mutagenicity or teratogenicity

All sampling and testing methods for the plant are anticipated to be identical to those outlined in the project work plan, dated 26 November, 1979. Any deviations are noted herein.

References

1. Gerstle, R., and J. Richards. Industrial Process Profiles for Environmental Use. EPA-600/2-77-023d, U.S. Environmental Protection Agency, Cincinnati, OHIO, February 1977.
2. Letkiewicz F., Chemicals Which Have Been Tested for Neurotoxic Effects. EPA-560/1-76-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1976. 1332 pp.
3. Markle, R.A., Fentiman, A.F., Steadman, T.R. and R.A. Mayer. An Assessment of the Treatment and Control of Wastes From the Manufacture and Use of Potentially Toxic and Hazardous Organic Chemicals. U.S. Environmental Protection Agency, (Patelle Columbus Laboratories Contract Number 68-02-1323). Cincinnati, OHIO, June 1974. 290 pp.

4. Watkins, DR. Review of Industrial Organic Chemicals Processes for Potentially Toxic Materials. Contract Number 68-03-2579. Environmental Protection Agency, Cincinnati, Ohio, August, 1978.
5. STANDARD INDUSTRIAL CLASSIFICATION MANUAL, Executive Office of the President / BUREAU OF THE Budget, 1976. pp 615.
6. Dorigan, J., Fuller, B. and R. Duffy. Scoring of Organic Air Pollutants Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals. Contract Number 68-02-1495, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1976. 331 pp.
7. Fairchild, E. J. Registry of Toxic Effects of Chemical Substances. Contract Number 210-75-0034, U.S. Department of Health, Education and Welfare. 1977 edition.
8. Merck and Co., The Merck Index 9th Edition, 1976.

9. Barret, William J., et al, Waterborne Wastes of the Paint and Inorganic Pigments Industries, National Environmental Research Center Office of Research and Development U.S Environmental Protection Agency, Cincinnati, OH 45268
10. Datagraphics Inc., Inorganic Chemicals Industry Profile (Updated), Environmental Protection Agency, July, 1971.

SURVEY DATA SHEETS

I. NAME

B1475

DATE OF
SUMMARY

NAME

PHONE

NAME OF COMPANIES

MRC PERSONNEL

David Dunn and David Vaneck

PHONE 513-268-3411

PHONE

EPA PERSONNEL

PHONE

PHONE

STATE PERSONNEL

PHONE

PHONE

INDUSTRY TYPE

Stainless steel, ingot, billet, bar, rod and
wire manufacture and processing (SIC 3312)

PORTION OF PROCESS TO BE SAMPLED

Outfall 001- total plant
discharge

II.

PROCESS DESCRIPTION

Scrap stainless steel and other alloying
metals are melted to form ingots which are cold
or formed into billets, bars, rods or wires

II. Con't.

Raw materials and amounts Scrap steel (majority), alloy materials

Fuels Natural gas and #2 fuel oil

Products and amounts 7000 T/year

Operating Cycle:

Check: Batch _____ Semi-Continuous ☒ Cyclic _____

Timing of batch or cycle _____

Best time to sample Anytime

Length of Operating day 24 hours

Length of operating week 7 days

Scheduled shutdowns 6/29 - 7/14 entire plant

Other melt shop remains down for 2 additional weeks

III.

WASTEWATER TREATMENT PLANT DESCRIPTION: No actual WWTP.

Combination contact/non-contact treatment. Basic discharge is non-contact cooling

Chemicals added and amounts Only spot treatment

Handles rainfall runoff? Yes

Includes sanitary waste, flow City

Source of plant intake water City water

Hydraulic retention time: Thru plant _____
Thru treatment unit operations N.A.

Recent treatment plant performance N.A.

III. Con't.

NPDES permit parameters: SS (197 #/day), Ni (4.9 #/day),
Hex Cr (43 #/day), Total Cr (4.5 #/day), Fe (6.8 #/day), Org (20 mg/l)

Final effluent flow rate: Flow rate equal to 0.5 MGD

List of potential pollutants: See attached sheet.

Recent analyses available? No

Sampling point description Sample at manhole (accessible
by ladder, <12' head) three separate 2 ft tiles meet
and mix at this manhole and are discharged (maximum).

Use automatic sampler? yes

Electricity available yes (110V)

Extension cord and type of outlet? _____

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

Item	Plant	MRC	Item	Plant	MRC
Safety glasses	✓	✓	Dust masks		
Goggles			Vapor masks		
Side shields	✓		Air purifying		
Face shields			Air supply		
Hard hats	✓	✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes	✓	✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
			First aid	✓	✓

B. SAMPLE SITE

1. Smoking restrictions None
2. Vehicle traffic rules 16 mph
3. Possible set-up/clean-up facilities? Labor room - guardhouse
4. Evacuation procedures None
5. Alarms None (Wed 1:00 p.m. alarm test)
6. Hospital location Information available
7. Hospital Phone _____
- Emergency Numbers See guardhouse, in-plant clinic

V. Plant Entry

- A. Plant Requirements Regulate at guardhouse. Pick-up
plans

Special time constraints: None

- B. MRC Agreement C

- C. Potential Problems _____

VI. SAMPLING HANDLING

A. Ice availability See guard on lead stores

B. Sample splitting requested yes

Describe 1 gal to each with grab

C. Nearest airport: Information available

D. Chemical available: H_2SO_4 _____

HNO_3 _____

$NaOH$ _____

VII Field Test Schedule *Information Available*

<div>Time</div> <div>Day</div>	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

Justification for Toxic compound selection

An analysis of each production process was undertaken to evaluate those pollutants which could potentially be present in the process effluent. Emphasis was placed on pollutants potentially present due to production and/or subsequent wastewater treatment.

This analysis typically involved first a compilation of information from respective NPDES permit files. This information, yielding location, type or types of processes, general flow diagrams, etc., was then applied to the list of references for each preliminary report. These additional references yielded information regarding reactants, products, byproducts, general unit operations employed and their parameters, plant specific information where known, experience with similar plants or industries, and finally, actual wastewater characterization data for each industry type.

Possible pollutant sources in the process wastewaters included water as a product of combustion or other process reaction, direct contact cooling water, product wash water, reactor washout wastes, condenser and scrubber water which has contacted either products or reactants, non-contact cooling water which may be contaminated due to process flange leaks, etc and finally, pollutants which may be produced as a result of the wastewater treatment system unit operations.

The analysis protocol for Phase I calls for automatically monitoring NPDES parameters, phenol, cyanide, inorganic ions and 76 elemental compounds. Therefore, organic compounds are the major output of this exercise.

No formal consideration was given to possible background contamination; eg. plant intake waters, as the program is concerned with the contribution emanating from a particular production point source.

The list of organic compounds finally generated was evaluated to determine the toxicity of its members."

As stated in the project work plan, those compounds suspected to be particularly toxic are to be semi-quantified, whenever possible, with the remainder of the list scanned for via mass spectrometry.

The toxicity evaluation parameters were as follows:

Any lethality rating < 500 mg/kg	→ semi-quantify
Any identified carcinogenicity	→ semi-quantify
Any identified mutagenicity	→ semi-quantify
Any identified teratogenicity	→ semi-quantify
Any known toxic decomposition products	→ semi-quantify
None of the above	→ qualify via M. S.

Plant B1475 is engaged in stainless steel manufacture. Although most of the outfall is non-contact cooling water, a significant portion is direct-contact cooling. Effluents typical to steel manufacturing are expected here.

B 147 S
SUSPECTED POLLUTANTS

Carbon tetrachloride*

1,1,1-Trichloroethane

Chloroform*

Chlorophenol*

2,4-Dichlorophenol*

Ethylbenzene

Pentachlorophenol*

Phenol*

Tetrachloroethylene*

Toluene*

Xylene*

Benzene*

* To be semi-quantified due to potential toxicity, carcinogenicity,
mutagenicity or teratogenicity

All sampling and testing methods for the plant are anticipated to be identical to those outlined in the project work plan, dated 26 November, 1979. Any deviations are noted herein.

References

1. Gerstle, R., and J. Richards. Industrial Process Profiles for Environmental Use. EPA-600/2-77-023d, U.S. Environmental Protection Agency, Cincinnati, OHIO, February 1977.
2. Letkiewicz F. Chemicals Which Have Been Tested for Neurotoxic Effects. EPA-340/1-76-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1976. 1332 pp.
3. Markle, R.A., Fentiman, A.F., Steadman, T.R. and R.A. Mayer. An Assessment of the Treatment and Control of Wastes From the Manufacture and Use of Potentially Toxic and Hazardous Organic Chemicals. U.S. Environmental Protection Agency (Attelle Columbus Laboratories Contract Number 68-02-1323). Cincinnati, OHIO, June 1974. 290 pp.

4. Watkins, DR. Review of Industrial Organic Chemicals Processes for Potentially Toxic Materials. Contract Number 68-03-2579. Environmental Protection Agency, Cincinnati, Ohio, August, 1978.
5. STANDARD INDUSTRIAL CLASSIFICATION MANUAL, Executive Office of the President / BUREAU of the Budget, 1976. pp 615.
6. Dorigan, J., Fuller, B. and R. Duffy. Scoring of Organic Air Pollutants Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals. Contract Number 68-02-1495, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1976. 331 pp.
7. Fairchild, E. J. Registry of Toxic Effects of Chemical Substances. Contract Number 210-75-0034, U.S. Department of Health, Education and Welfare. 1977 edition.
8. Merck and Co., The Merck Index 9th Edition, 1976.

1. Draft Development Document for the Iron and Steel manufacturing Point Source Category, Effluent Guidelines Division, Office of Water and Waste Management, U.S. Environmental Protection Agency, October, 1979.

APPENDIX C

PHASE III SAMPLING AND ANALYTICAL METHODS

C.1 INTRODUCTION

The chemical analysis scheme implemented in Phase III was designed to collect sufficient data to screen 28 effluent samples and 22 sediment samples for the presence of chemical species known or suspected to be present, and to identify as many of the other compounds as possible within the time and economic constraints. Samples were collected in Maryland and Virginia; in Maryland 8 effluent and 5 sediment samples were taken, and in Virginia 20 effluent and 17 sediment samples were taken.

The objectives of the Phase III chemical and physical analysis scheme were as follows:

1. Quantitative analysis of NPDES parameters, anions and metals;
2. Semiquantitative analysis of organic compounds known or suspected to be present in the samples (based on an engineering evaluation of the plant production processes), identified as being potentially toxic;
3. Qualitative analysis of other organic compounds suspected to be present in the sample, but not particularly toxic;
4. Qualitative analysis of other unknown organic compounds, detected in the sample by gas chromatography/mass spectrometry (GC/MS);

5. Determination of the potential for organic compounds in the samples to accumulate in the food chain; and
6. Presentation of the data in a format consistent with other Bay Program studies.

This appendix contains a detailed description of the methods employed and the purpose and goal of each test. Examples are included to brief the reader on the thought process involved in analyzing the data.

C.2 FIELD SAMPLING METHODOLOGY

Sampling was designed to collect sufficient water to determine if the data generated by the chemical and physical analysis protocol were sufficient to measure the type and amount of pollutants being discharged at the site. Sampling was conducted in Maryland by MRC personnel with the help of Maryland Department of Health personnel. Typically, sampling was performed by a two-man crew, starting at mid-morning and lasting about three hours. In Virginia, effluents and sediments were sampled by State Water Control Board personnel.

Table C.2-1 presents a field sampling logistics checklist that was used by the sampling crews. Listings include analyses to be conducted, volume required, type of container, preservative used, and analysis laboratory. This checklist (filled out prior to the site visit) was used to organize the crew during sample splitting and packing and details the final destination of each bottle of effluent.

C.2.1 Maryland Sites

In order to minimize sample contamination, grab samples were collected in Teflon®-lined buckets and transferred to one of two compositing containers. One sample was collected and placed in a 190-liter (50-gallon) plastic container. Aliquots were removed from this container for analysis of NPDES parameters and inorganic species. The second sample was collected and placed in a 19-liter (5-gallon) glass container. Aliquots were removed from this container for analyses of all organic compounds. By segregating the samples in different types of containers, contamination from the collection vessels, such as plasticizers or leached metals, was avoided. The glass vessel was packed in ice during the sampling period to reduce the possibility of loss of volatile compounds and biodegradation.

TABLE C.2-1. FIELD SAMPLING LOGISTICS CHECKLIST FOR PHASE III PLANTS

PLANT CODE _____

SAMPLING TEAM _____

Sampling required at site	Analysis	Volume required	Container	Preservative	Ship to
_____	pH	100 mL	Beaker	None	Analyze on site
_____	Flow	--	--	--	Determine at site
_____	Filtration	150 mL	Filter apparatus	--	Perform on site
_____	Plant spill potential	--	--	--	Determine at site
_____	Fish/Daphnia	25 gal	5 5-gal cubitainers	4°C	EG&G - Wareham
_____	Algae (freshwater)	5 gal	1 5-gal cubitainers	4°C	EG&G - Pensacola
_____	Sheepshead/mysid/oyster larvae	25 gal	5 5-gal cubitainers	4°C	EG&G - Pensacola
_____	Algae (marine)	5 gal	1 5-gal cubitainers	4°C	EG&G - Pensacola
_____	HERL/RTP	1 gal	1 1-gal glass	4°C	Shabeg Sandhu-EPA-HERL/RTP
_____	Battelle, Columbus	15 gal	3 5-gal cubitainers	4°C	Columbus, Ohio
_____	Battelle, Duxbury	5 gal	1 5-gal cubitainer	4°C	Duxbury, Mass.
_____	Annapolis - AFO will supply prepreserved bottles for NPDES and anion analysis				Annapolis Field Office
_____	Filtered ICAP metals	50 mL	Plastic	4°C, 5 mL HNO ₃	Annapolis Field Office
_____	Unfiltered ICAP metals	50 mL	Plastic	4°C, 5 mL HNO ₃	Annapolis Field Office
_____	Filtered Hg analysis	100 mL	Plastic	4°C, 5 mL HNO ₃	Annapolis Field Office
_____	Unfiltered Hg analysis	100 mL	Plastic	4°C, 5 mL HNO ₃	Annapolis Field Office
_____	Volatile organics	80 mL	2 40-mL glass vials	4°C	Monsanto Research Corporation
_____	Nonvolatile organics	3 gal	3 1-gal glass	4°C	Monsanto Research Corporation
_____	Extra sample/bioaccumulation	1 gal	1 1-gal glass	4°C	Monsanto Research Corporation
_____	Bioassay (Ames/CHO)	3 gal	3 1-gal glass	4°C	Monsanto Research Corporation
_____	TOC	500 mL	Glass	4°C, H ₂ SO ₄ , pH<2	Monsanto Research Corporation
_____	Special analysis				
_____	Direct water injectables	No separate sample required			
_____	Aldehyde analysis	1 gal	1 1-gal glass	4°C, 1% sodium bisulfite	Monsanto Research Corporation
_____	Nitrogen-phosphorus detector FID/GC	No separate sample required			
_____	Derivatization	No separate sample required			
_____	Sulfur analysis	250 mL	Plastic	4°C	Monsanto Research Corporation
_____	Inorganics	1 L	Plastic	4°C	Monsanto Research Corporation

C.2-2

Grab samples for purgeable organics analysis were taken by collecting a sample in a Teflon®-lined bucket and then filling the 40-mL vial by completely immersing it in the bucket. These samples were collected at the beginning and ending of the sampling period. Samples were hermetically sealed immediately after sampling, then labeled and stored at 4°C until shipment. The vials were shipped in ice to maintain this temperature.

After the sampling period was completed, the crew thoroughly mixed the sample in the composite vessels with a Teflon®-coated rod and then divided the effluent into appropriate bottles. Preservatives were added to the bottles when needed to maintain sample integrity. Samples were carefully labeled with the type of analysis to be run, the plant code, and the name of the analytical laboratory that was to perform the analysis. Samples were then packed in ice for shipment. Once packing was complete, samples were shipped that day by air freight to the appropriate laboratory and were normally delivered in less than 24 hours.

In addition to the samples taken, other pertinent information was collected. Discussions with plant representatives gave the team leader an indication of the treatment operation for the day (i.e., upset or normal operation). Temperature and other weather factors that may have affected the samples or sampling procedures were also noted. Flow measurements were requested from the plant in order to determine the total discharge into the Chesapeake Bay basin. All significant sampling procedure deviations were also noted.

C.2.2 Virginia Sites

During the month of April 1981 effluent from 20 plants discharging into the James and Elizabeth Rivers were sampled by Virginia State Water Control Board (SWCB) personnel. At each plant a carefully cleaned 110 gallon linear polyethylene tank was rinsed

with the effluent and then filled using a submersible pump with nonreactive fittings. Aliquots of effluent samples used for chemical analyses were taken from the tank in the field. The remaining effluent was transported back to the SWCB facility for fish bioassays and Microtox® tests. When no fish bioassays were performed, a 13-gallon linear polyethylene container was filled with effluent and samples were taken from this container. SWCB personnel took dissolved oxygen, pH, temperature, and conductivity/salinity readings at each plant, and the instantaneous flow rate was obtained from the plant recorder. Plant operators were also queried as to any current treatment problems at their facility. All clean sample containers were rinsed three times with effluent prior to filling, with the exception of the filtered metals and oil and grease containers. The samples taken at each plant were as follows:

1. Four 1-gallon amber glass bottles for nonvolatile organics.
2. Two 40-mL glass vials with Teflon septa for volatile organics--these vials were filled while submerged in effluent in a stainless steel bucket to prevent air bubbles.
3. One 500-mL amber glass bottle for TOC--fixed with H_2SO_4 such that the pH was less than 2.
4. Two 125-mL wide-mouth plastic bottles, one for ion chromatographic analysis and one for total sulfur.
5. One 1-gallon cubitainer for BOD, TSS, NO_2^- , NO_3^- , ortho-phosphate, and color.
6. Four 1-quart cubitainers, one each for:

- (a) Total Kjeldahl nitrogen, total phosphorus, NH_3 , fixed with H_2SO_4 such that the pH was less than 2.
- (b) Total metals, fixed with HNO_2 such that the pH less than 2.
- (c) CN^- , fixed with NaOH such that the pH was greater than 12.
- (d) Phenol, fixed with H_2SO_4 such that the pH was less than 2, then 5 mL CuSO_4 added.

To sample for filtered metals, a Büchner funnel apparatus and portable electric pump were used. Initially, the funnel, flask, and quart cubitainer were rinsed with deionized water. Then 150 mL of effluent were measured in a graduated cylinder; and vacuum-filtered through a pre-weighed 0.45 μm paper filter on the Büchner apparatus. The filter was removed from the Büchner funnel, sealed in a plastic Petri dish for shipment to MRC, and analyzed for metals associated with solids in the sample. The filtrate was poured into the quart cubitainer and acidified with HNO_3 to a pH less than 2.

At selected plants, several additional samples were also collected:

1. One 1-quart cubitainer for COD, fixed with H_2SO_4 such that the pH was less than 2.
2. One 1-quart cubitainer for sulfite.
3. One 1-quart glass jar for oil and grease.
4. One 5-gallon cubitainer of effluent, sent to the E.G.&G. Bionomics laboratory in Pensacola, Florida for mysid shrimp bioassay.

All samples were hermetically sealed with stretch tape, wrapped in bubble packing, placed on ice in sealed coolers, and mailed to the appropriate locations for analysis.

For the sediment sampling, SWCB personnel collected sediments in the vicinity of eleven of twenty outfalls. A joint Virginia Institute of Marine Science--Maryland Geological Survey crew collected sediments at another six outfalls. No sediments were collected for the three remaining outfalls due to substrate limitations at each site.

The object of the sediment sampling program was to perform the same set of chemical tests on fine-grained sediments near each outfall which were performed on the effluent itself. If persistent toxic substances found in the analysis of the effluent were also found in the sediment, a possible link could be formed between the discharge of this chemical and its appearance in the environment.

Sediment sampling goals were straightforward: obtain a fine-grained sediment sample as closely as possible to each outfall. Equipment used in the sampling were either the 6 in. x 6 in. or 9 in. x 9 in. Ponar sediment grab sampler. The undisturbed top 3 cm of each sediment sample were removed with a stainless steel scoop and placed in specially cleaned glass one-liter jars supplied by the Virginia Institute of Marine Science. Jar lids were lined with a sheet of Teflon plastic. After labeling, the samples were frozen by placing them in coolers with dry ice. The samples were shipped on dry ice via air freight to Monsanto Research Corporation's lab in Dayton, Ohio.

C.3 NPDES PARAMATERS

In Phase III, the Central Regional Laboratory of EPA analyzed grab samples for NPDES parameters. The test, method, and quality control performance are given in Table C.3-1.

TABLE C.3-1. NPDES PARAMETERS ANALYZED BY EPA IN PHASE III

Test	Method	Average QC accuracy, %
BOD	Winkler/Probe [1]	101.0
COD	Standard Methods [1]	104.9
Turbidity	Standard Methods [1]	- ^a
Nitrate	Automated Cadmium Reduction [2]	104.4
Total dissolved phosphorus	Automated Colorimetric Ascorbic Acid Reduction [2]	100.8
Total phosphorus	Automated Colorimetric Ascorbic Acid Reduction [2]	104.3
Ortho-phosphate	Automated Colorimetric Ascorbic Acid Reduction [2]	100.8
Ammonia	Automated Phenate Colorimetric [2]	109.2
Phenol	Distillation/Colorimetry [1]	98.0
Cyanide	Distillation/Pyridine Colorimetric [1]	99.0
Chromium VI	Colorimetric, Diphenylcarbazide [1]	- ^a
Dissolved mercury	Cold Vapor [2]	98.2
Total mercury	Cold Vapor [2]	101.5
TKN	Automated Phenate Method [2]	94.1
Color	Colorimetric, Platinum Color Units [1]	- ^b
TSS	Standard Methods [1]	103.2
Fluoride	Electrode [2]	100.0

^aBlanks indicate no QC data reported.

^bNot applicable.

- [1] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater (14th Edition). American Public Health Association, Washington, D.C., 1977.
- [2] U.S. EPA, Methods for Chemical Analysis of Water and Wastes. EPA-625/6-76-003a, National Environmental Research Center, Cincinnati, Ohio, 1976.

C.4 ION CHROMATOGRAPHY FOR ANALYSIS OF ANIONS

C.4.1 Method

Ion chromatography (IC) was used to measure the anions F^- , Cl^- , SO_3^{-2} , and SO_4^{-2} in the plant effluent samples. Ion chromatography is a highly selective instrumental technique for rapidly determining ionic species. The technique is based on well-established ion-exchange principles used in a novel way that allow electrical conductance to be used to detect and quantitate ions which are selectively eluted from a chromatographic column.

This novel adaptation of ion exchange principles involves the use of a background ion suppressor column to eliminate or minimize the ionic character of the mobile phase. In the case of anion analyses, sodium carbonate and/or bicarbonate in the mobile phase is converted to the weakly conductive carbonic acid, while the anions to be measured are converted to strongly conducting acid forms. As the anions elute from the chromatographic column, the change in electrical conductance of the mobile phase is measured and recorded as a function of time on a strip chart recorder or data system. For relatively clean waters, detection limits of low ppm or ppb levels can be attained.

Both qualitative and quantitative data were generated in the analysis. The retention times (time of elution from the column after sample introduction) are correlated with individual anions and can be used to identify the anion. However, it is important to note that very high anion concentrations can result in significant shifting of retention times for the anions. Suitable quality control/quality assurance standards must be analyzed along with the unknowns to validate the qualitative identifications.

To protect the separator column from the effects of overloading and contamination, a guard column was used which contained the

same ion exchange resin as the separator column. The guard column is replaced or regenerated as necessary and insures consistent response from the separator column.

Because of the diverse nature of the plant effluents in this program and the complexity of the sample matrix, the analytical procedures were optimized to yield maximum sensitivity for all sample types. Samples were run in several dilutions to obtain an acceptable response for each anion of interest. Samples were analyzed for the anions F^- , Cl^- , SO_3^{-2} , and SO_4^{-2} using a Model 10 Dionex ion chromatograph which utilized a 3 mm x 150 mm pre-column, a 3 mm x 500 mm anion separator column as the analytical column, a 6 mm x 250 mm anion suppressor column and 0.003M $NaHCO_3$ /0.0024M Na_2CO_3 in deionized water as the eluent, with an operating pressure of 240 psi to 360 psi. Sample volumes of 0.1 mL were injected into the chromatograph.

The only sample preparation involved filtration through a 0.45-micron nitrocellulose filter. In the cases where the chloride and sulfate concentrations exceeded the working range of the instrument, samples were diluted with deionized water.

Calibration curves were generated for each anion by plotting peak height of the anion versus concentration of that anion in standard anion solutions. Four different concentrations of each ion were plotted and response factors calculated using linear regression analysis. Peak heights obtained from samples were converted to concentration units using these response factors. Spiked samples were run to verify peak identification and recovery. To assure proper quantitative measurements, replicate analyses and measurement of a sufficient number of quality control/quality assurance standards were also performed.

The analysis was performed without further sample preparation. Typical calibration curves for the anions detected are given in Figures C.4-1 through C.4-4.

The analytical method was the basic Dionex procedure for anions. Quantitative measurements were made by comparing the chromatographic response for the unknown with the response for known concentrations of anions in deionized water. Initially, after the filtration step, single analyses were performed on the samples as received. Because of the high concentrations of chloride and sulfate ions, additional analyses were performed on samples diluted in deionized water.

Figure C.4-5 shows a representative ion chromatographic pattern for a typical sample. Particularly notable are the peak shapes of the two major components: chloride (major early eluting component) and sulfate (major later eluting component). The greater broadening of the peak characteristic of sulfate anion than the peak characteristic of chloride anion is due partially to differences in anion size and charge. Ion size and charge determine the ion interaction with the resin of the chromatographic column. Ions that have a charge that can be polarized toward the functional group of the resin will have a slower rate of exchange between the resin and mobile phase. Therefore, ions such as sulfate will elute later and the chromatographic peaks will be broader than those for chloride or fluoride ions. Additional peak broadening and tailing can result from overloading the active sites of the resin. An additional result of resin overload is a decrease in retention time of the eluting components as samples are processed in sequence.

C.4.2 QA/QC for Anion Analysis

To assure proper performance of the ion chromatograph during the sequence of analyses, the electrical conductivity response of the

C.4-4

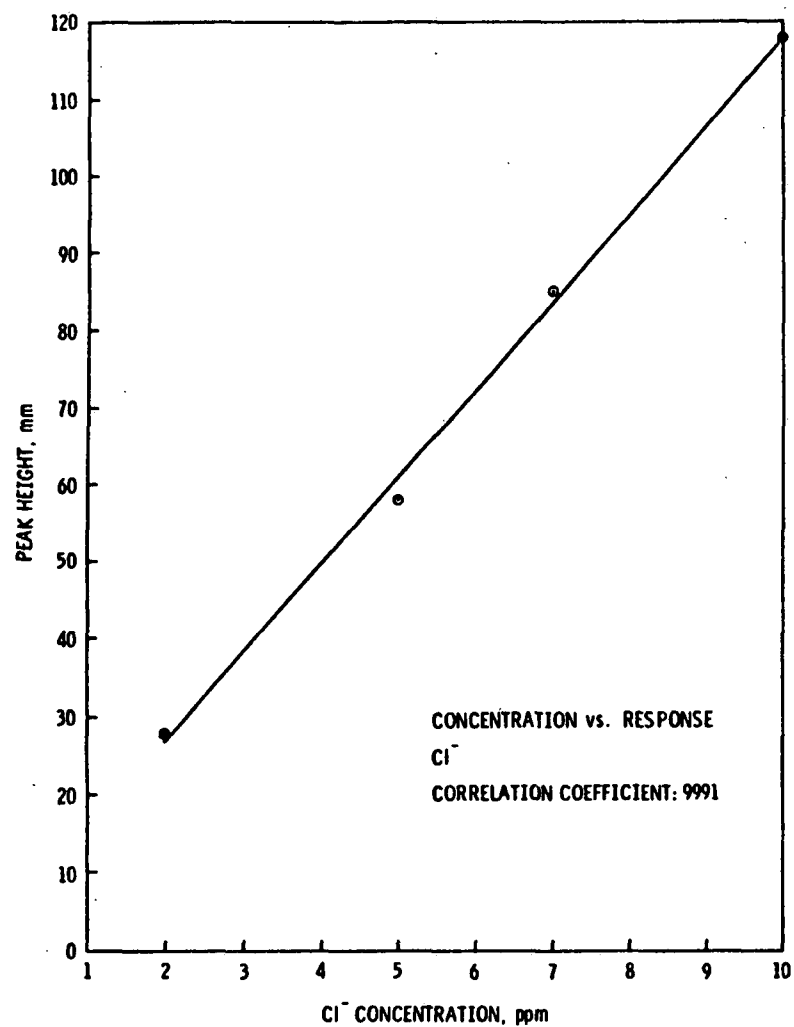


Figure C.4-1. Peak height vs. chloride ion concentration.

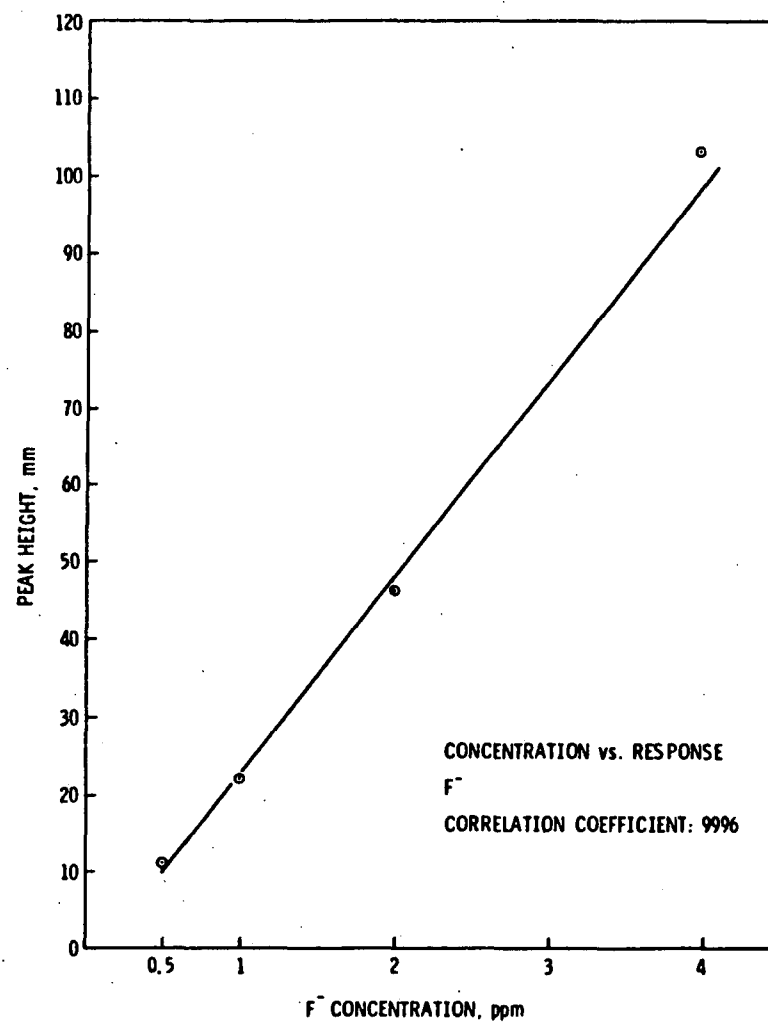


Figure C.4-2. Peak height vs. fluoride ion concentration.

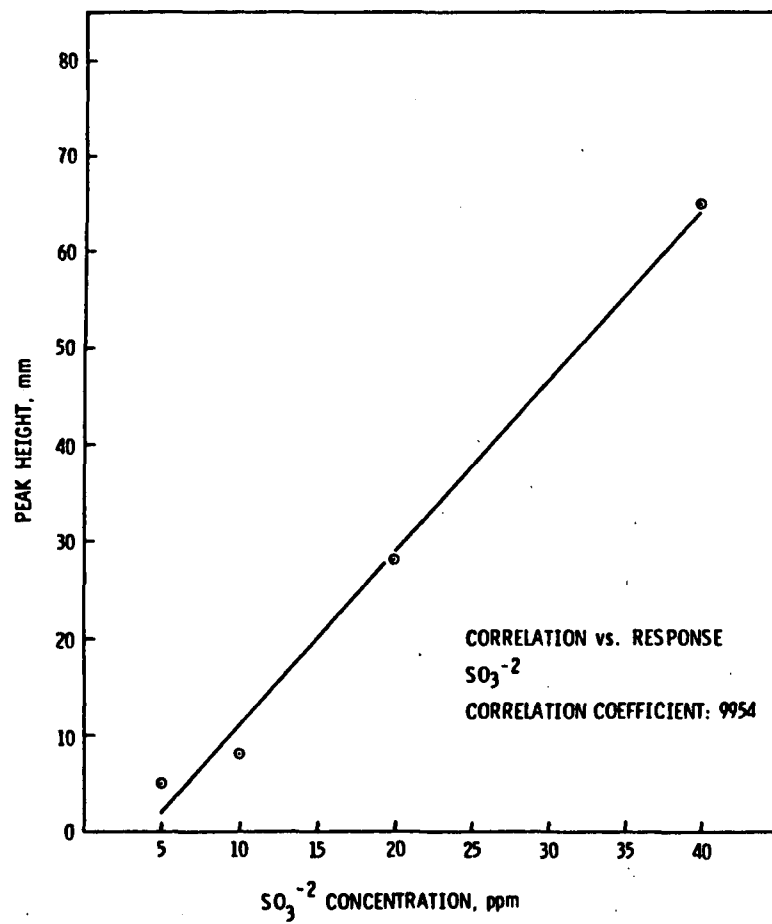


Figure C.4-3. Peak height vs. sulfite ion concentration.

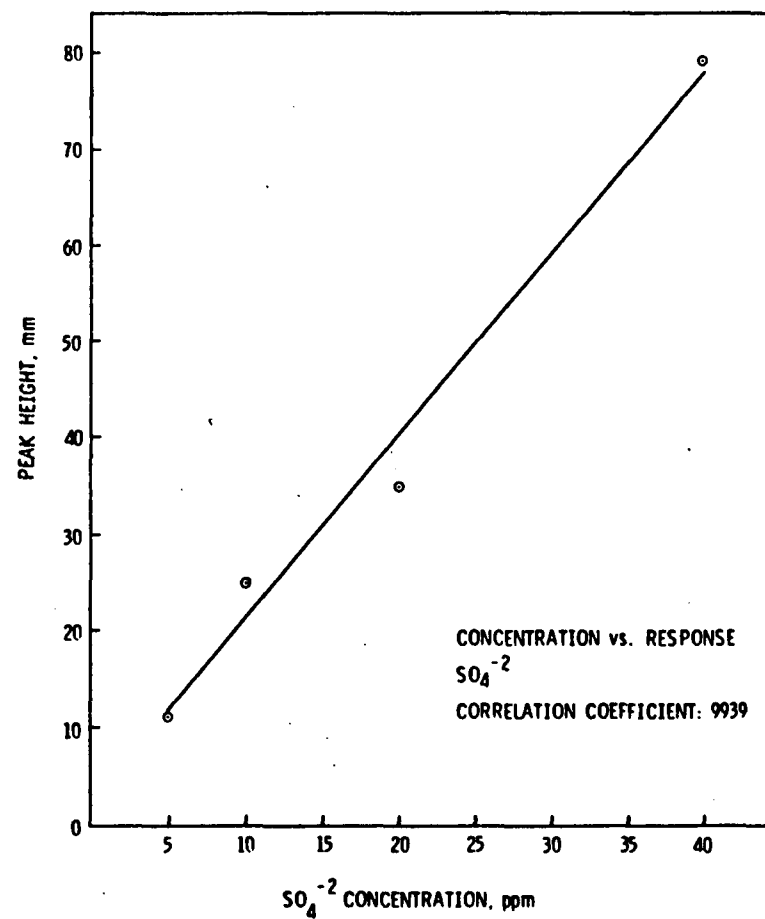


Figure C.4-4. Peak height vs. sulfate ion concentration.

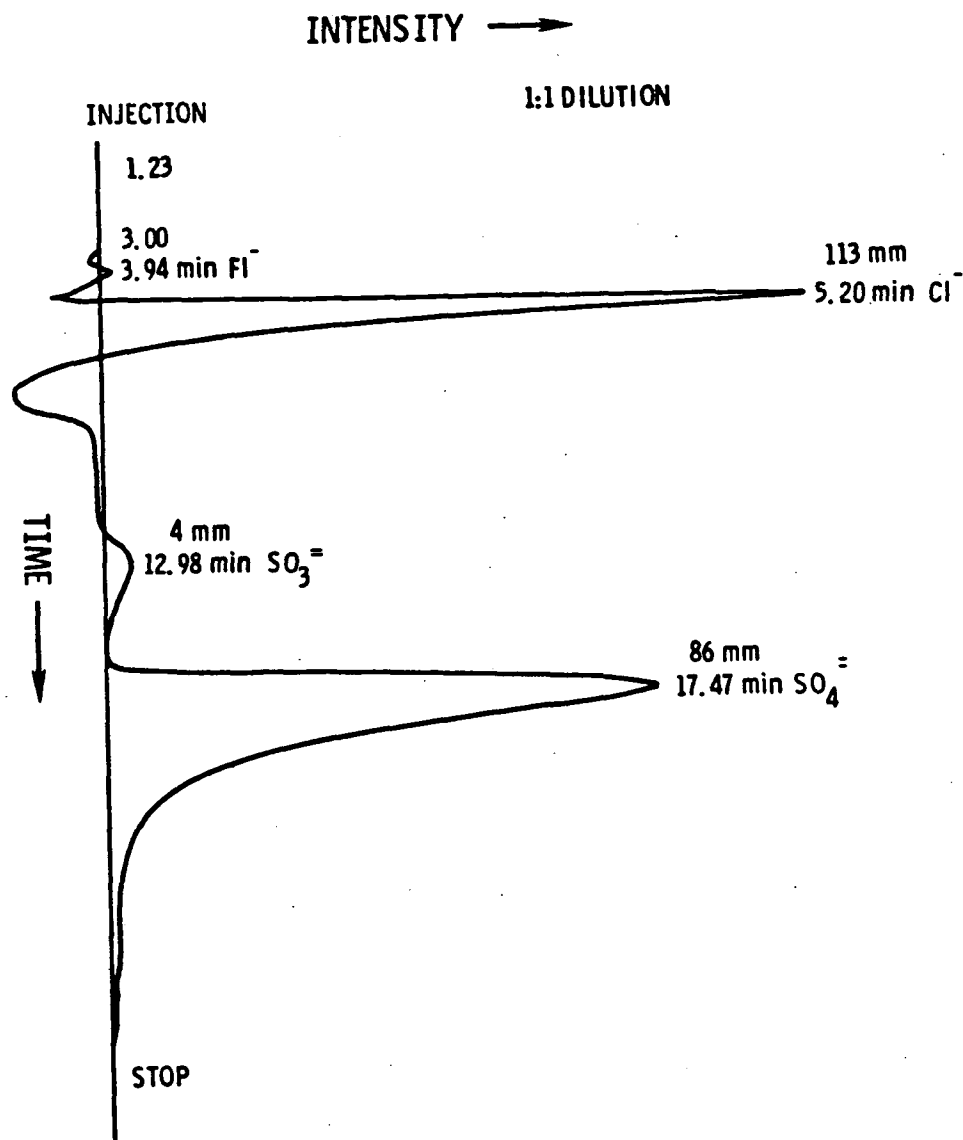


Figure C.4-5. Ion chromatographic pattern for typical sample.

detector was determined using standard conductance solution and the column quality was verified. The system was found to be within the Dionex instrument specifications for the Model 10.

Analyses of deionized water blanks were performed with each set of samples. The calibration curves were prepared prior to the analysis of each set of samples and a representative standard solution of anions was checked after the analysis of each set of samples.

C.5 ICAP SPECTROSCOPY FOR METALS ANALYSIS OF BAY SEDIMENT

C.5.1 Introduction

Inductively Coupled Argon Plasma (ICAP) was used to measure the concentration of 24 metals in the Chesapeake Bay sediment samples. The ICAP technique is a very powerful method for the determination of metals in solution. The ICAP has several advantages over conventional flame atomic absorption, such as simultaneous, multi-element determinations, high temperature with low background, and linearity often extending over 5 orders of magnitude in concentration. In routine analyses, the ICAP has detection limits similar to flame AA for most transition metals and alkaline earths and far superior detection limits for refractories and nonmetals.

C.5.2 Sample Prep

Approximately 0.5 g (weighed to 0.1 mg) of the freeze dried sediment sample was prepared for analysis by the Parr Teflon Bomb method using 12 mL of concentrated Ultrex HNO_3 as the digestion media. After digestion, the sample was filtered to remove any insoluble particulates (probably silicates) and diluted to a known volume. At this point, the sample was analyzed with no further preparation.

C.5.3 Analysis

ICAP operations followed the manufacturers instructions. In addition, the guidelines given in EPA interim ICAP method 200.7 were followed. The Parr Bomb blank was subtracted from the sample values. Background correction was used to compensate for a shift caused by high concentrations of sodium and aluminum. Also, interelement correction factors were used to correct for the spectral overlap of several metals caused by high levels of iron.

For equipment used, operating conditions and elemental wavelengths, see Tables C.5-1, C.5-2, and C.5-3, respectively.

TABLE C.5-1. EQUIPMENT USED

Spectrometer	JY48P 1 meter focal length
Computer	Digital Equipment Corporation PDP-1103 16K memory
Terminal	LA120 DECWRITER
Nebulizer	Meinhard glass concentric
RF generator	Plasma-Therm Model 2500D
Pump	Gilson, Model HP-4

TABLE C.5-2. SYSTEM OPERATING CONDITIONS

Incident RF power	1.4 kW
Reflected RF power	≤ 5 W
Coolant Ar flow rate	16 L/min
Auxiliary air flow rate	0.6 L/min
Nebulizer pressure	18 psi
Sample uptake rate	~ 0.75 mL/min
Observation height	14 mm above load coil
Number of integrations	3
Integration time	10 s
Background correction	+0.5 A
Sample flush time	60 s

TABLE C.5-3. WAVELENGTHS

Element	$\lambda, \text{\AA}$	Element	$\lambda, \text{\AA}$	Element	$\lambda, \text{\AA}$
Ag	3,280.68	Cr	2,677.16	P	2,149.14
Al	3,082.15	Cu	3,247.54	Pb	2,203.53
B	2,089.59	Fe	2,382.04	Sb	2,068.33
Ba	2,335.27	Mg	2,795.53	Si	2,516.11
Be	3,130.42	Mn	2,576.10	Sr	4,077.71
Ca	3,158.87	Mo	2,020.30	Ti	3,349.41
Cd	2,265.02	Na	3,302.37	V	3,102.30
Co	2,286.16	Ni	2,316.04	Zn	2,138.56

C.5.4 QA/QC for ICAP Analysis

To insure that the instrument was operating properly, reference standards were analyzed at a frequency of 10% (one reference standard with every 10 samples). Five samples were digested in duplicate. Duplicate samples showed high relative percent differences for a number of elements. This is indicative of problems with sample homogeneity. Na, Si, and Zn had consistently high relative percent differences. The high differences in Zn values are probably due in part to contamination from filters used in digestion and from contact with polyethylene tubing and bottles. Two samples were to be spiked at the time of digestion. However, from the low recoveries obtained for sample B143S, it appears that the spike was inadvertently omitted.

Sample C158D had acceptable recoveries where the unspiked sample value was less than 10 times the concentration of the spike. It should be noted that variations in sample homogeneity will have a large bearing on percent recoveries.

C.6 ANALYSIS OF PURGEABLE ORGANICS

C.6.1 Bellar Purge and Trap Technique For Purgeable Organics

The 40-mL vials were analyzed for volatile organics by the purge and trap method using a standard packed-column GC/MS [3]. This method was designed for trace-level volatile organics contained in a wide variety of water sources. For quantitative determinations the method is limited to organic compounds that are less than 2% soluble in water and that boil below 200°C. Most compounds boiling above 200°C would be found in the methylene chloride extracts of the water, the analysis of which is described later.

This method of volatiles analysis is useful at levels from 1 µg/L to 2,500 mg/L. At concentrations exceeding 2,500 mg/L, flooding of the chromatographic column and nonlinear detector responses generally occur. It typically works well except on those samples where foaming is a problem. Water entering the trap causes non-quantitative trapping and severe gas chromatographic interferences.

C.6.2 GC/MS Analysis of Purgeables

The two vials in which the effluent samples were collected were stored at 4°C. Before analysis the contents of the vials were composited in an ice bath and returned to the original vials, again with no headspace. The samples were first allowed to warm to room temperature to prepare them for analysis. Next, the plunger from a 5-mL syringe equipped with a valve was removed. The sample to be analyzed was poured into the syringe body, with the valve closed, until the sample overflowed. The syringe plunger was then replaced and the residual air and excess volume of sample

[3] Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants. Final Draft Report, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 1977.

was removed. Internal standards (1,4-dichlorobutane and bromochloromethane) were added to the water sample in the syringe by means of a 10 μ L syringe inserted through the valve at the delivery end of the 5 mL syringe. The 5 mL of sample was introduced into the purging device and sparged with high purity helium at a rate of 40 mL/min at room temperature for 10 minutes. The purged organics were sorbed onto a 2.7 mm x 15.2 cm (1/8 in. x 6 in.) stainless steel tube packed with 6.4 cm (4 in.) of Tenax GC (60/80 mesh) and 3.2 cm (2 in.) of type 15 silica gel (35/60 mesh). The tube was then desorbed by backflushing at 180°C for 10 min onto the head of the chromatographic column which was maintained at -40°C. The sequence used consisted of analyzing a particular tube from an organic-free water sparge, and then using the same tube for the sparging of an effluent sample, so that the immediate history of the tube was known.

Samples were analyzed using a modified Hewlett-Packard 5983 GC/MS, operated in the positive ion, electron impact mode, with a 5934A data system. The following parameters describe the system.

- 6 ft x 2.7 mm stainless steel column
- 0.2% Carbowax 150 on 80/100 mesh Carbopak C
- Flow rate, 30 mL/min helium
- Initial temperature, -40°C
- Time at initial temperature, 0 min
- Heating rate, 8°C/min
- Time at final temperature, 5 min
- Glass jet separator and glass-lined transfer lines, 260°C
- Electron energy, 70eV
- Emission current, 300 μ a
- Source temperature, 200°C
- A/D rate, 5 measurements/0.1 amu; scan rate 41.6 amu/s
- Mass spectrometer scan delay, 2 min

The GC/MS data were examined for priority pollutant compounds and for other substances present in identifiable amounts. The EPA volatile priority pollutants (Consent Decree compounds) are listed in Table C.6-1, along with their typical retention times, major masses, and associated intensities. To indicate the presence of a priority pollutant compound by GC/MS, three conditions must be met. First, the characteristic ions for the compound (see Table C.6-1) must maximize in the same spectrum. Second, the time at which the peak occurs must be within a window of ± 1 min for the retention time of the compound. Finally, the ratios of the ion intensities must agree with the relative intensities given in Table C.6-1 within $\pm 20\%$.

Substances not identified in the specific search for priority pollutants were sought in a "wide scan" mode. In this procedure, mass spectra are obtained for peaks not accounted for in the previous search, and the ions observed are compared with those listed in the Eight Peak Index to produce a tentative identification [4]. The amounts of these substances are estimated by comparing their total ion areas with those of similar compounds for which standards are available, or of the internal standards, assuming a similar ionization cross section (hence semiquantitation).

C.6.3 Example of Quantitation Performed in Purgeables Analysis

From the mass spectral analysis of a standard mixture one obtains the response of the major ions of each species relative to those of the internal standards present in the mixture. For example:

[4] Eight Peak Index of Mass Spectra, Vol. III, 2nd Ed., Mass Spectrometry Data Center, AWRE, Aldermaston, Reading, United Kingdom, 1974.

TABLE C.6-1. TYPICAL RETENTION TIMES AND CHARACTERISTIC IONS OF VOLATILE CONSENT DECREE COMPOUNDS MEASURED IN THE PURGE AND TRAP TECHNIQUE

Retention time, min	Compound	EI ions (relative intensity)	Ion used to quantify
6.2	Chloromethane	50(100); 52(33)	50
6.4	Dichlorodifluoromethane	85(100); 87(33); 101(13); 103(9)	85
6.1	Bromomethane	94(100); 96(94)	96
6.9	Vinyl chloride	62(100); 64(33)	62
8.1	Chloroethane	64(100); 66(33)	64
10.3	Methylene chloride	49(100); 51(33); 84(86); 86(55)	84
12.7	Trichlorofluoromethane	101(100); 103(66)	101
13.4	1,1-Dichloroethylene	61(100); 96(80); 98(53)	61
13.1	Bromochloromethane (IS)	49(100); 130(88); 128(70); 51(33)	130
14.2	1,1-Dichloroethane	63(100); 65(33); 83(13); 85(8); 98(7); 100(4)	63
15.2	<i>trans</i> -1,2,-Dichloroethylene	61(100); 96(90); 98(57)	61
15.1	Chloroform	83(100); 85(66)	83
16.2	1,2-Dichloroethane	62(100); 64(33); 98(23); 100(15)	62
17.0	1,1,1-Trichloroethane	98(100); 99(66); 117(17); 119(16)	97
17.6	Carbon tetrachloride	117(100); 119(96); 121(30)	117
17.9	Bromodichloromethane	83(100); 85(66); 127(13); 129(17)	83
-	bis-Chloromethyl ether	79(100); 81(33)	79
19.3	1,2-Dichloropropane	63(100); 65(33); 112(4); 114(3)	63
19.6	<i>trans</i> -1,3-Dichloropropene	75(100); 77(33)	75
20.5	Trichloroethylene	95(100); 97(66); 130(90); 132(85)	130
20.3	Dibromochloromethane	129(100); 127(78); 208(13); 206(10)	129
20.9	<i>cis</i> -1,3-Dichloropropene	75(100); 77(33)	75
20.7	1,1,2-Trichloroethane	83(95); 85(60); 97(100); 99(63); 132(9); 134(8)	83
21.3	Benzene	78(100)	78
-	2-Chloroethylvinyl ether	63(95); 65(32); 106(18)	106
22.8	Bromoform	171(50); 173(100); 175(50); 250(4); 252(11); 254(11); 256(4)	173
25.9	1,1,2,2-Tetrachloroethene	129(64); 131(62); 164(78); 166(100)	166
24.9	1,1,2,2-Tetrachloroethane	83(100); 85(66); 131(7); 133(7); 166(5); 168(6)	83
25.4	1,4-Dichlorobutane (IS)	55(100); 90(30); 92(10)	55
27.3	Toluene	91(100); 92(78)	91
28.2	Chlorobenzene	112(100); 114(33)	112
30.0	Ethylbenzene	91(100); 106(33)	91
-	Acrolein	26(49); 27(100); 55(64); 56(83)	56
-	Acrylonitrile	26(100); 51(32); 52(75); 53(99)	53

<u>Compound Identified</u>	<u>Major ion</u>	<u>Peak area</u>	<u>Conc., µg/L</u>	<u>Rval₁</u>	<u>Rval₂</u>
(Int. Std.) Bromochloromethane	130	9,763	400	-	-
(Int. Std.) 1,4-dichlorobutane	55	14,271	400	-	-
Vinyl chloride	62	43,315	800	2.22	1.52
Chloroform	83	39,313	400	4.03	2.75
Benzene	78	69,903	400	7.16	4.90

The R values are calculated as follows, using chloroform for example:

$$R_1 = \frac{\text{Area chloroform, mass 83}}{\text{Area bromochloromethane, mass 130}} \times \frac{\text{Conc. bromochloromethane}}{\text{Conc. chloroform}}$$

$$= \frac{39,313}{9,763} \times \frac{400}{400} = 4.03$$

$$R_2 = \frac{\text{Area chloroform, mass 83}}{\text{Area 1,4-dichlorobutane, mass 55}} \times \frac{\text{Conc. 1,4-dichlorobutane}}{\text{Conc. chloroform}}$$

$$= \frac{39,313}{14,271} \times \frac{400}{400} = 2.75$$

The R values, obtained as above, are then employed to quantitate compounds identified in actual water samples, for example:

<u>Compound Identified</u>	<u>Major ion</u>	<u>Peak area</u>	<u>Rval₁</u>	<u>Rval₂</u>	<u>Conc., µg/L</u>
(Int. Std.) Bromochloromethane	130	9,741	-	-	400
(Int. Std.) 1,4-dichlorobutane	55	12,245	-	-	400
Chloroform	83	1,343	4.03	2.75	-
Benzene	91	2,681	7.16	4.90	-

The concentrations are calculated in the following manner, again using chloroform for an example:

$$\text{Chloroform Conc.}_1 = \frac{\text{Area chloroform, mass 83}}{\text{Area bromochloromethane, mass 130}} \times \frac{\text{Conc. Bromochloromethane}}{\text{Rval}_1 \text{ chloroform}}$$

$$= \frac{1,343}{9,741} \times \frac{400}{4.03} = 14 \text{ µg/L}$$

$$\text{Chloroform Conc.}_2 = \frac{\text{Area chloroform, mass 83}}{\text{Area 1,4-dichlorobutane, mass 55}} \times \frac{\text{Conc. 1,4-dichlorobutane}}{\text{Rval}_2 \text{ chloroform}}$$

$$= \frac{1,343}{12,245} \times \frac{400}{2.75} = 16 \mu\text{g/L}$$

$$\text{Average} = 15 \mu\text{g/L}$$

C.6.4 QA/QC for Purgeable Organics

The concentrations reported were measured relative to Supelco Standards A, B, and C, calculated as explained in the previous section. The absorption tubes used for trapping the volatile species were conditioned prior to use under vigorous conditions to eliminate carry-over from one sample to another. This was done by sparging organic-free water into a tube for 20 minutes, and then heating the tube for 1 hour at 200°C with helium flowing through it at 40 mL/min. In addition, each sample was analyzed using a tube that had been previously used for organic-free water, as mentioned in the section on analysis. The multiple blanks were averaged and used for background subtraction in calculating the results reported. The duplicate analyses of three samples that were performed gave an average percent deviation of ±21%.

C.7 EXTRACTABLE ORGANICS FROM EFFLUENTS

Figures C.7-1 through C.7-4 show the detailed scheme employed in work-up and analysis of the extractable organics fractions of the Phase III effluent samples.

C.7.1 Extraction Procedure

Figure C.7-5 is a facsimile of MRC's sample extraction QA/QC flow sheet used by the analyst to ensure that every element of the extraction has been performed. The circles were checked as each step of the procedure was performed.

For ease of handling, each 10-L sample was divided into four aliquots of 2.5 L, which were then spiked with deuterated recovery standards (listed in Table C.7-1). After allowing the spiked samples to equilibrate 0.5 hr, the pH of each aliquot was adjusted to ≥ 12 using 6% NaOH; each aliquot was then extracted with 100 mL of methylene chloride (CH_2Cl_2) followed by two additional 75 mL portions. For each extraction, the separatory funnels are manually shaken for 2 min (by the clock), and then allowed to

TABLE C.7-1. DEUTERATED RECOVERY STANDARDS ADDED TO 10-LITER EFFLUENT SAMPLE

Compound	Concentration, $\mu\text{g/L}$
Phenol- d_6 ^a	112
1,2-Dichlorobenzene- d_4	118
Biphenyl- d_{10}	102
Pyrene- d_{10}	99
Chrysene- d_{12}	83
Perylene- D_{12}	85

^aRecovered as Phenol- d_5 , due to exchange of the labile deuterium with protons from the water.

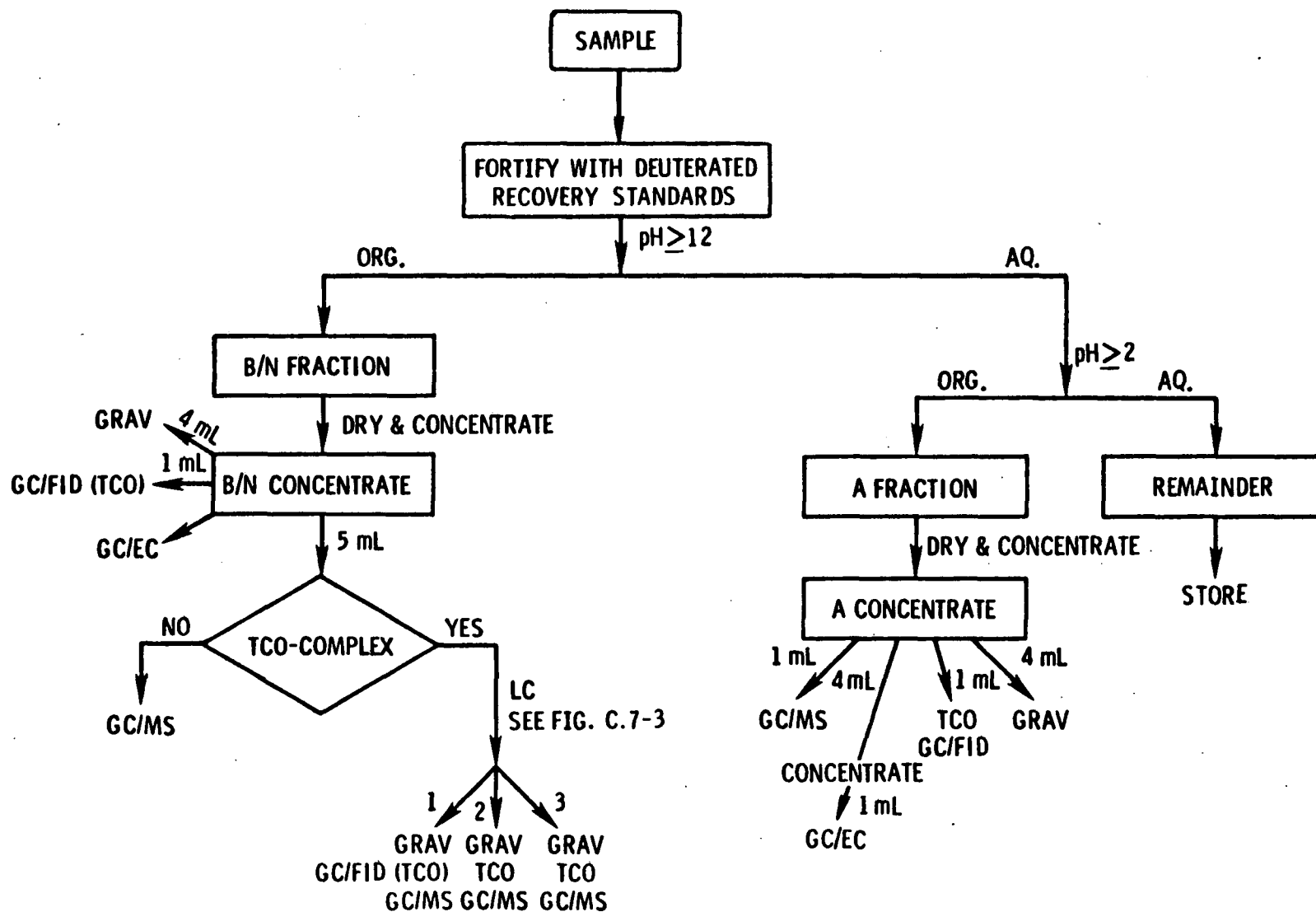


Figure C.7-1. Overall Phase III effluents analytical scheme.

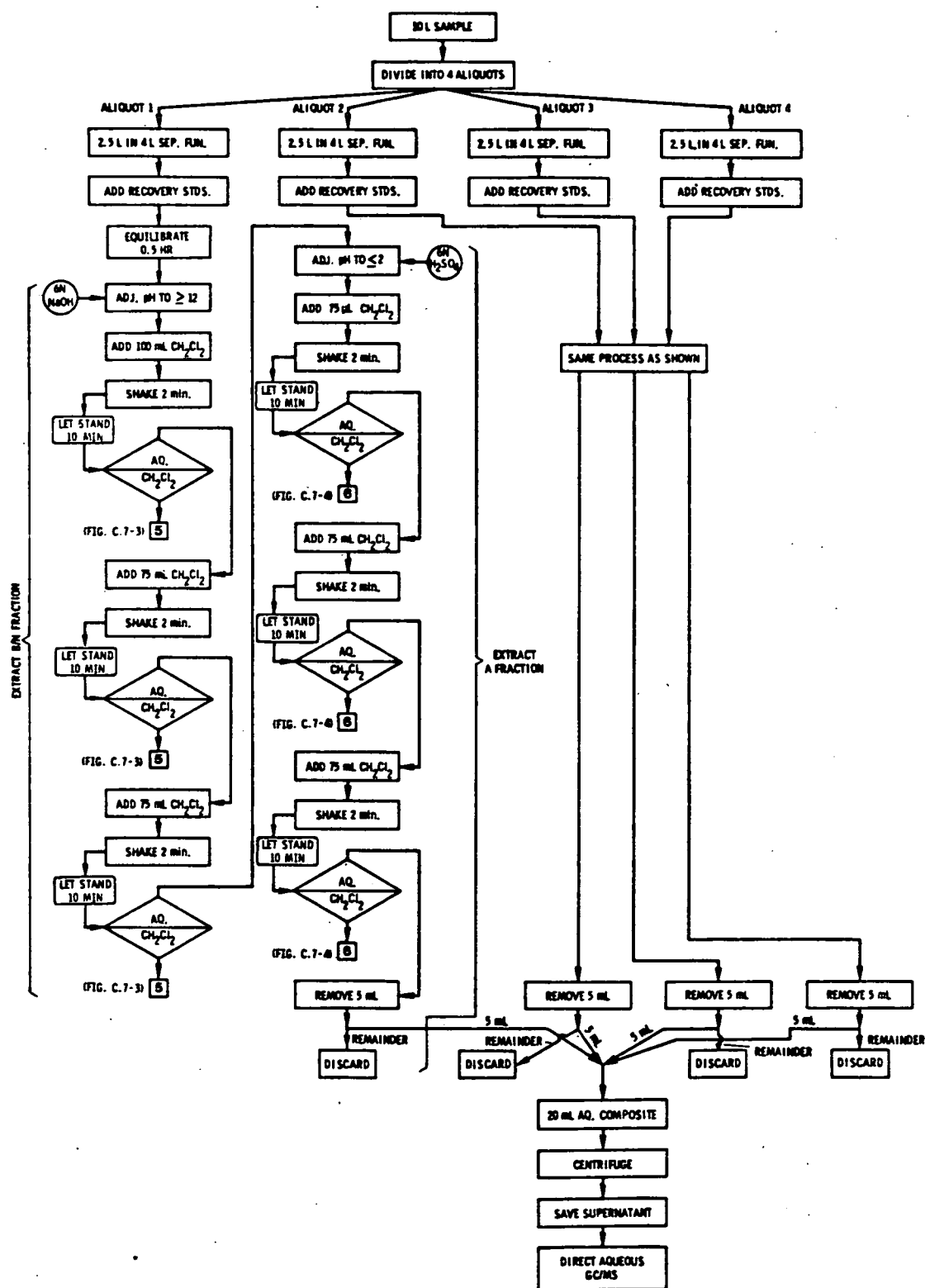


Figure C.7-2. Extraction procedure for Phase III effluent samples.

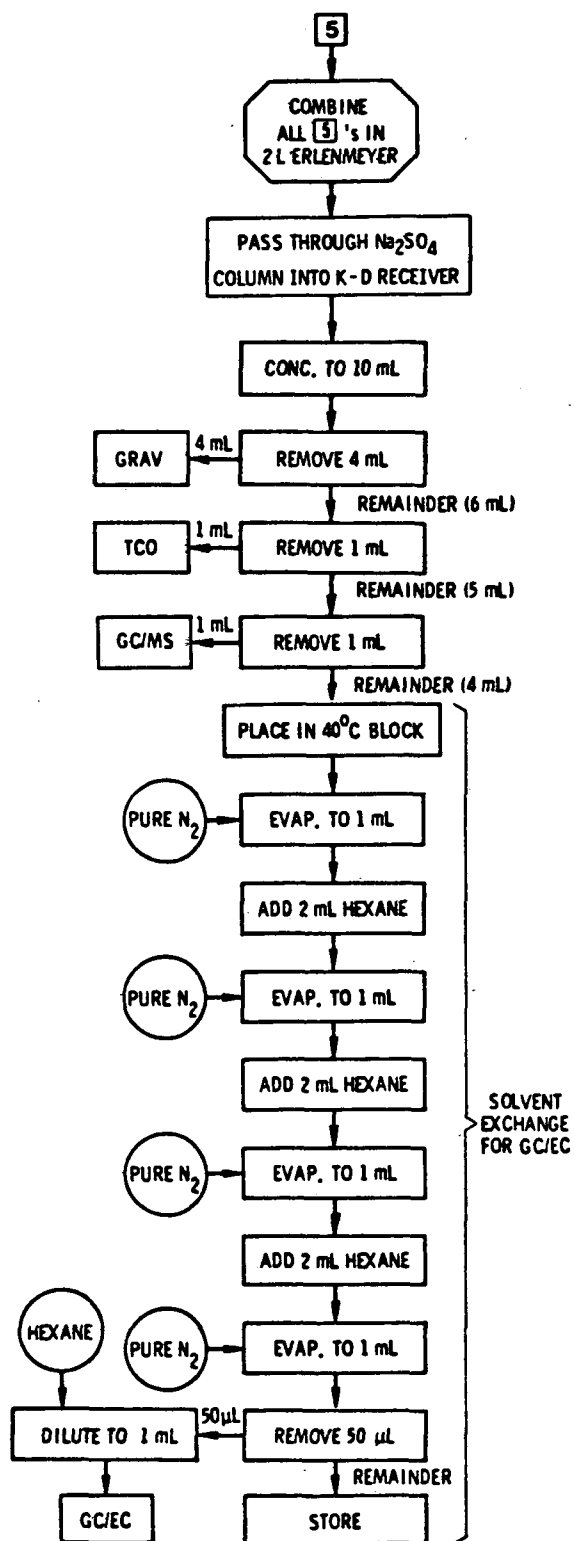


Figure C.7-3. Concentration and analysis scheme for base/neutral fraction.

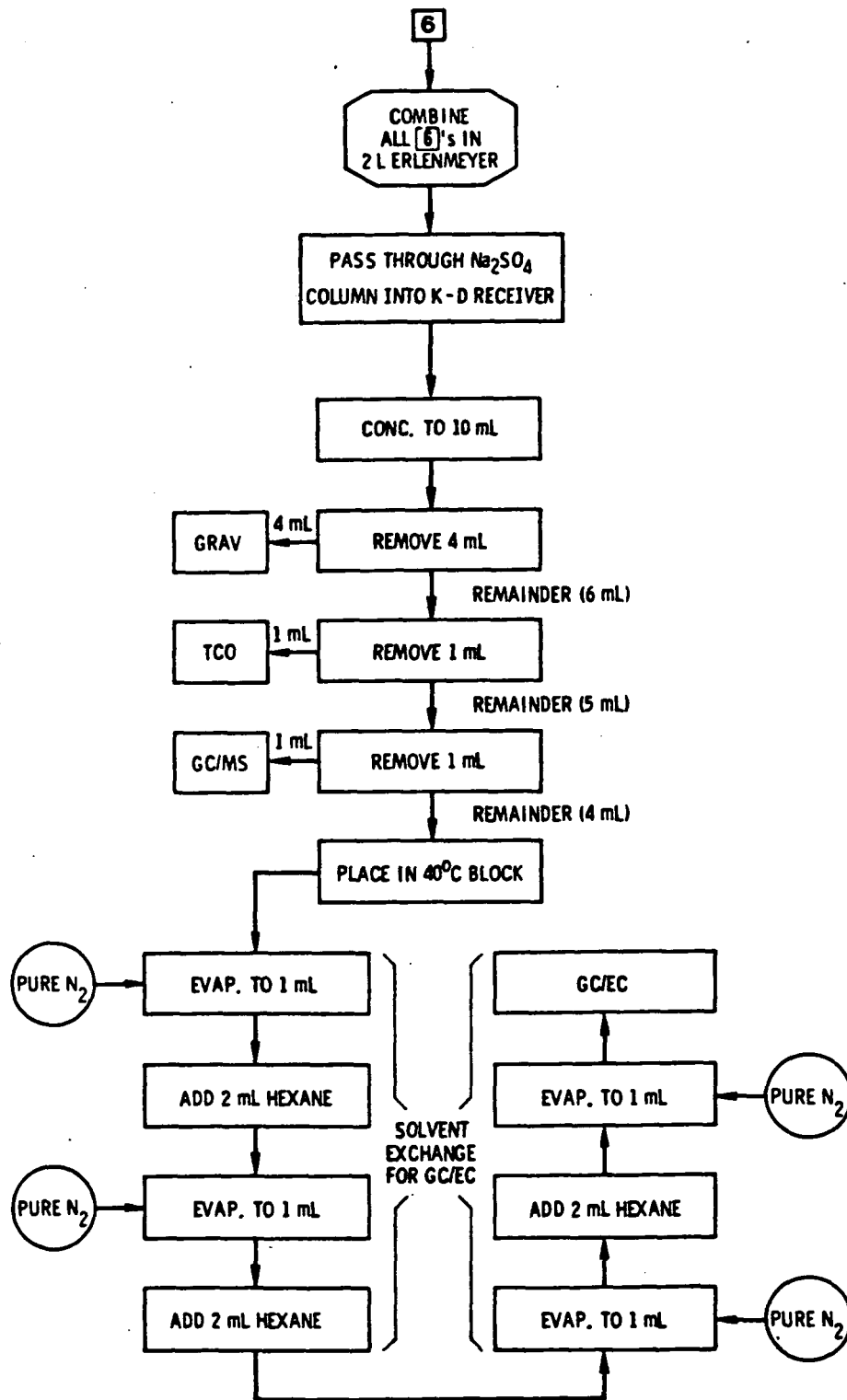


Figure C.7-4. Concentration and analysis scheme for acid fraction.

C.7-6

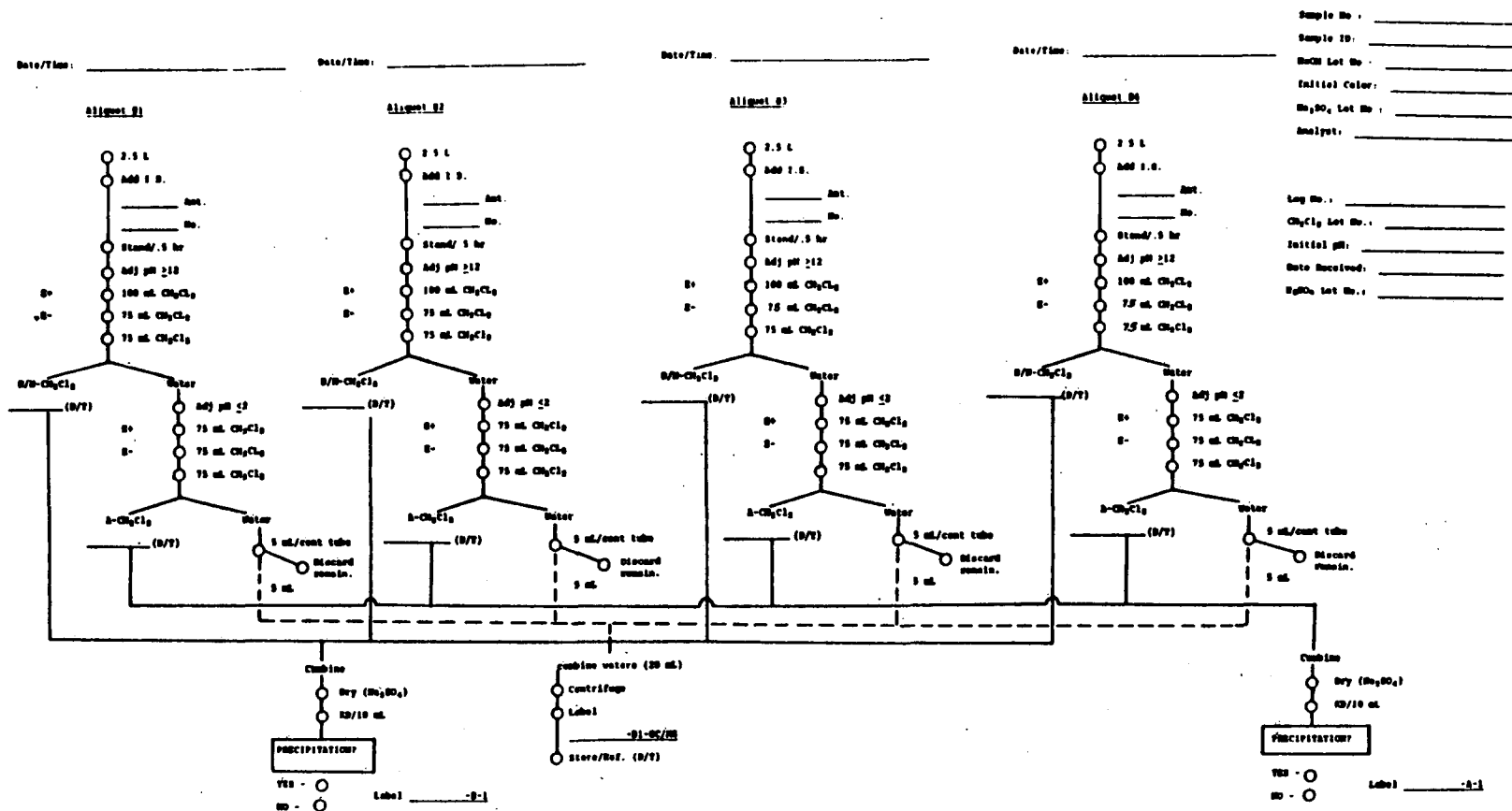


Figure C.7-5. Phase III extraction flow sheet.

stand a minimum of 10 min to complete separation of the liquid phases. The larger volume used in the initial extraction is to allow for the solubility of the solvent in the sample. The extracts were combined, dried over sodium sulfate, and concentrated to 10 mL using Kuderna-Danish evaporative concentrators, giving a 1,000-fold concentration of extractable base/neutral organics, assuming 100% extraction efficiency. Four mL of this 10 mL concentrate was removed for GRAV analysis and 1 mL each for TCO and GC/MS was stored in screw-cap vials with Teflon closures. The remaining 4 mL of concentrate was solvent exchanged with hexane and further concentrated to 1 mL for GC/EC analysis. The check sheets for these procedures are given in Figures C.7-6 through C.7-8.

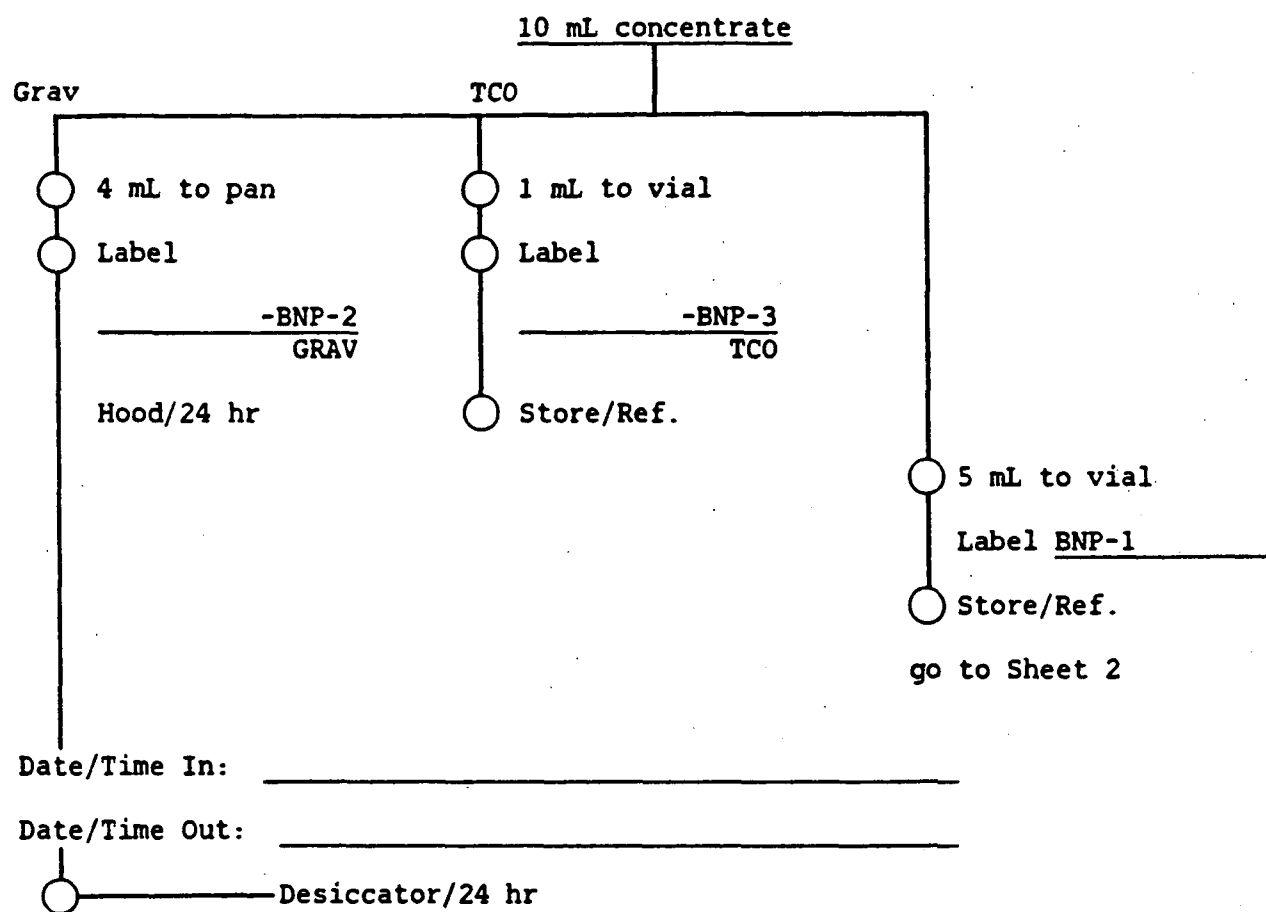
Each supernatant aqueous portion from the base/neutral CH_2Cl_2 extractions was acidified to $\text{pH} \leq 2$ using 6N H_2SO_4 , and extracted with CH_2Cl_2 (3 x 75 mL), as before. The combined acidic extracts were concentrated to 10 mL, giving an extractable acidic organics fraction enriched 1,000-fold from the original effluent, again assuming 100% extraction efficiency. Four mL of this 10 mL concentrate was taken for GRAV analysis while 1 mL each for TCO and GC/MS was stored, as above, for TCO and GC/MS analyses. The remaining concentrate was solvent exchanged with hexane and concentrated to 1 mL for GC/EC. The check sheets for these procedures are given in Figures C.7-6 through C.7-8.

C.7.2 Liquid Chromatographic (LC) Fractionation

None of the effluent samples that were part of the Phase III program required liquid chromatographic (LC) fractionation. However, in those cases where fractionation should be required based on TCO/TCG, the following procedures (graphically shown in Figure C.7-9) would be followed to improve identification of individual species.

Sample No.: _____ Date: _____

Color of extract: _____ Analyst: _____



Date/Time In: _____

Date/Time Out: _____

Pan and Sample: _____

Pan Tare: _____

Residue: _____

Figure C.7-6. Base/neutral extract flow sheet 1.

SIMPLE TCO

Sample No.: _____ Date: _____
(should contain -BNP-1)

Hexane Lot No.: _____ Analyst: _____

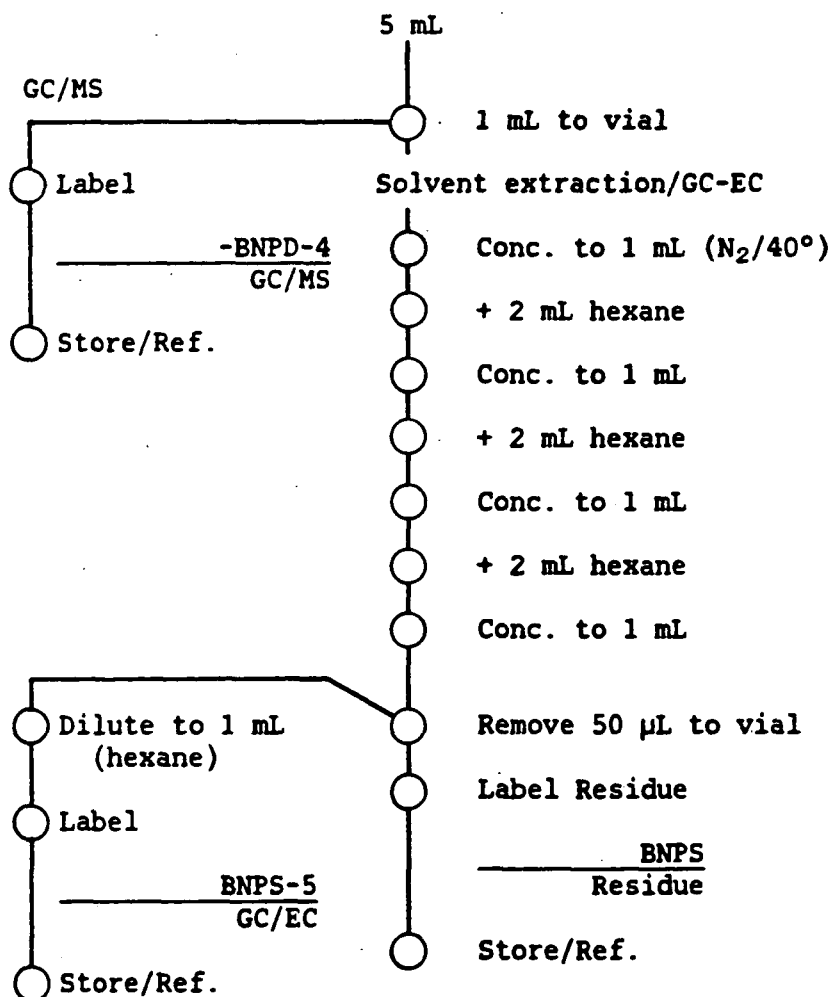


Figure C.7-7. Base/neutral extract flow sheet 2.

Sample No.: _____ Date: _____

Color of Extract: _____ Analyst: _____

Hexane Lot No.: _____

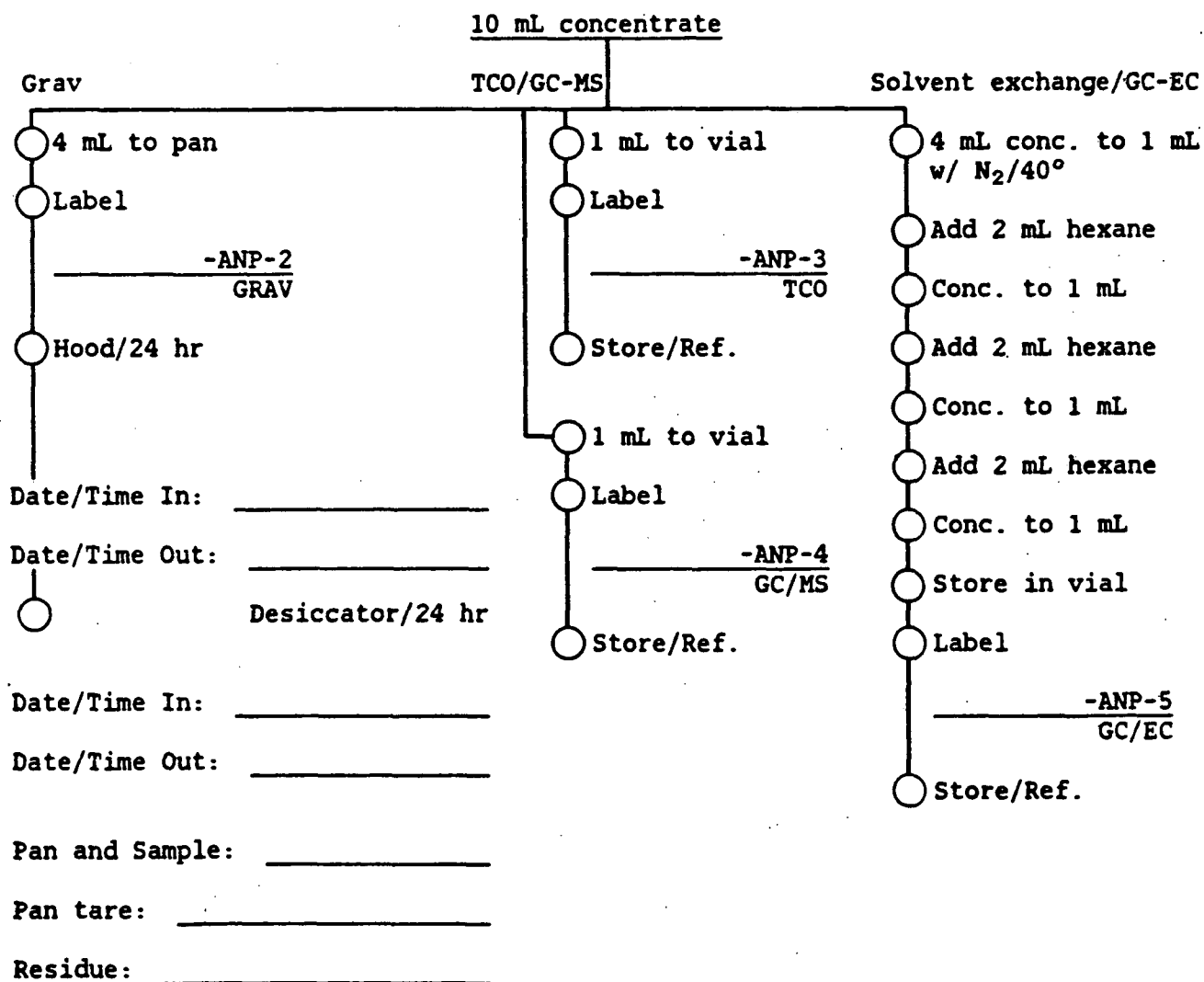


Figure C.7-8. Acid extract flow sheet.

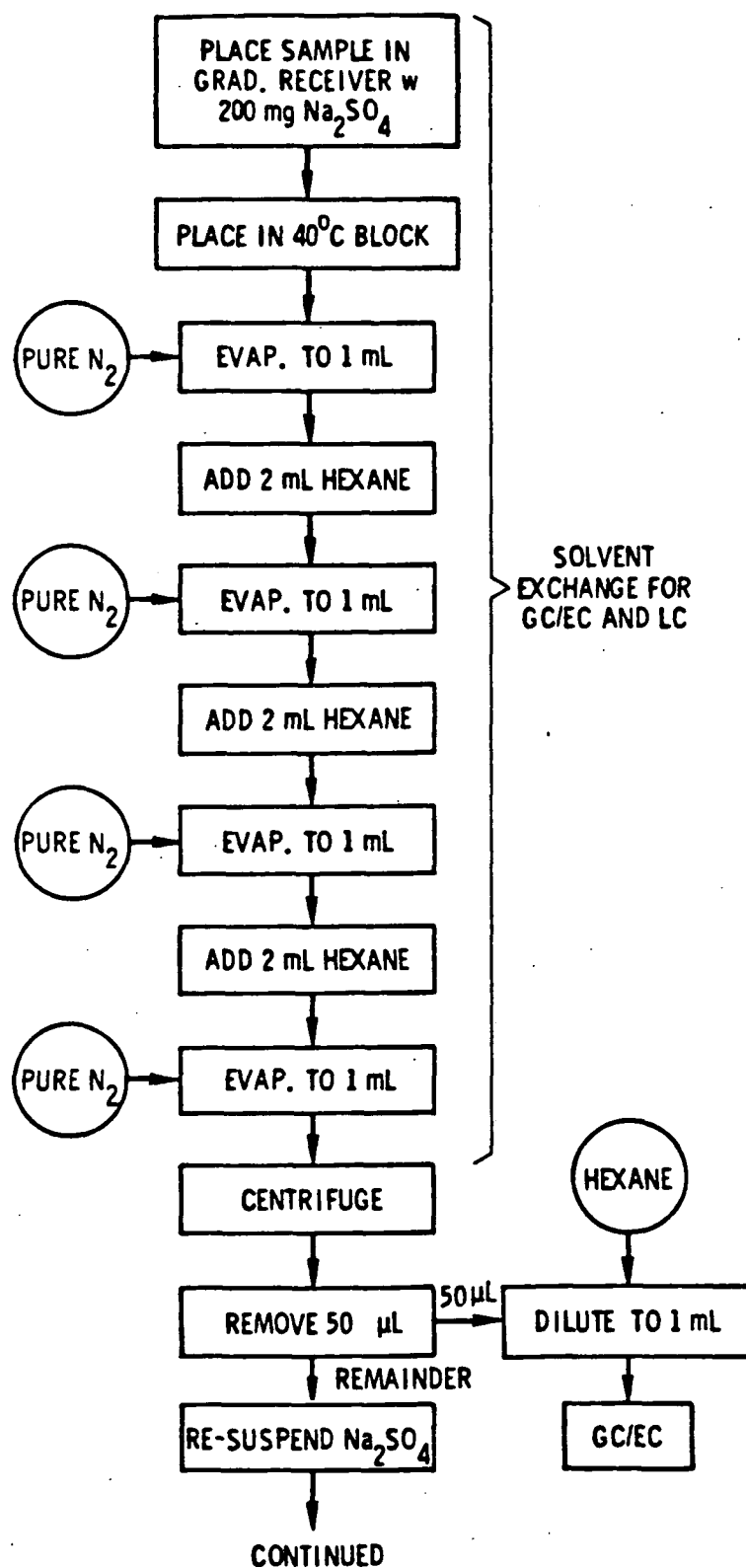


Figure C.7-9. Liquid chromatographic fractionation.

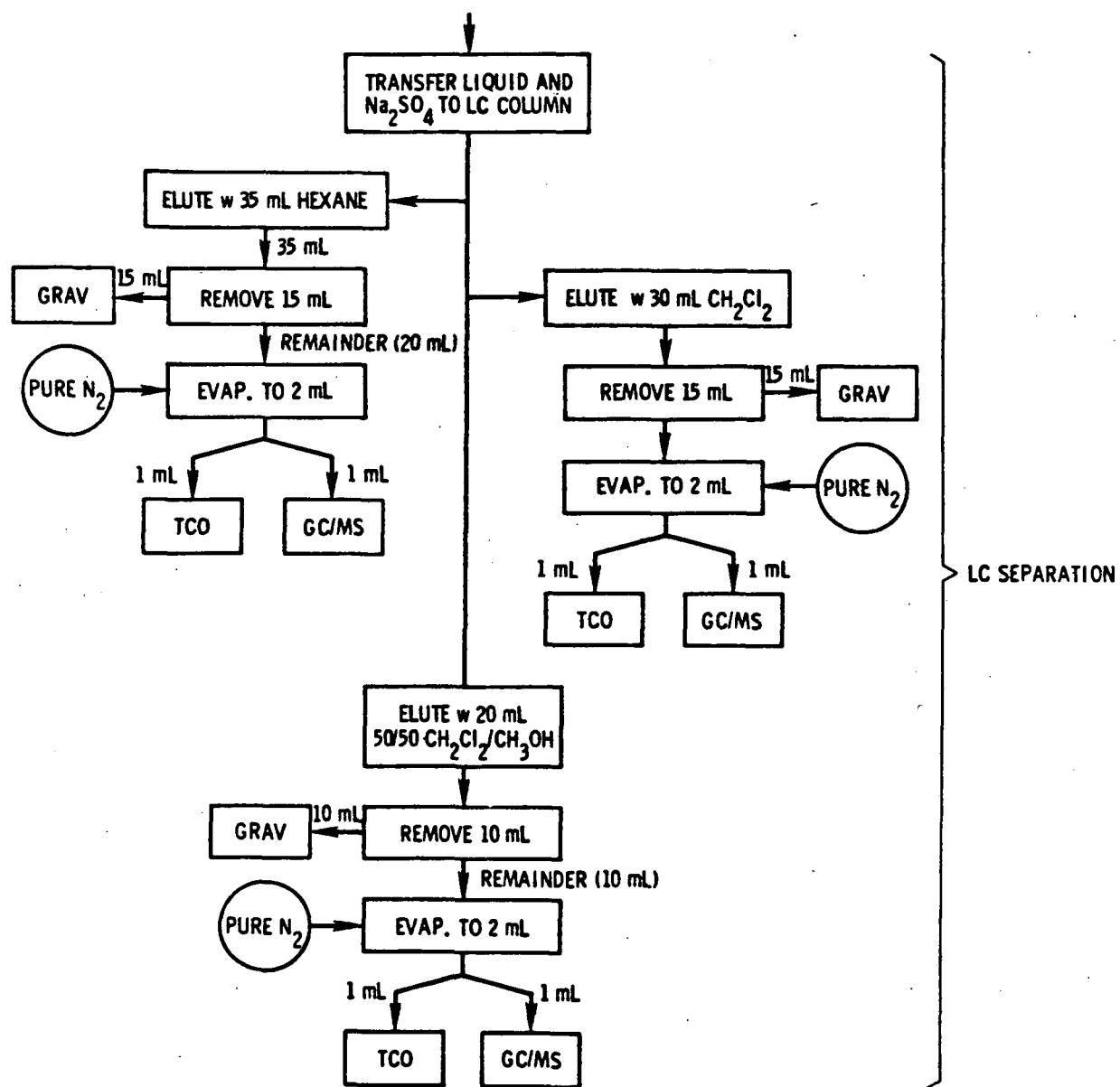


Figure C.7-9 (continued)

A 5-mL portion of the B/N concentrate remaining after the GRAV and TCO/TCG analyses is solvent-exchanged into hexane in the presence of sodium sulfate and concentrated to 1 mL. After removing 50 μ L for GC/EC analysis, the hexane concentrate was transferred as a slurry to a prepared silica gel column. Details of the column preparation are as follows:

Column: 200 mm x 10.5 mm ID, glass with Teflon stopcock, equipped with cooling water jacket.

Adsorbent: Davison, Silica Gel, 60-200 mesh, Grade 950 (available from Fisher Scientific Company) should be used. This material is cleaned prior to use by sequential Soxhlet extraction with methanol, methylene chloride, and hexane. The adsorbent is then activated at 110°C for at least 2 hr just prior to use, and cooled in a desiccator.

Drying Agent: Sodium sulfate (anhydrous, reagent grade).

Cleaned by sequential Soxhlet extraction for 24 hr each with methanol, methylene chloride, and hexane. The cleaned sulfate is dried for at least 2 hr at 110°C and cooled in a desiccator, just prior to use.

Procedure for Column Preparation: The chromatographic column, plugged at one end with a small portion of glass wool, is slurry-packed with 6.0 g of freshly activated silica gel in hexane. The total height of the silica bed, in this packed column, is about 10 cm. After packing the silica gel column, 3 g \pm 0.2 g of clean sodium sulfate is added to the top of the column and vibrated for 1 min to compact the column. The sodium sulfate is used to remove any remaining traces of water from the organic extract and/or the solvents used. Once the column is fully prepared, the pentane level in the column is dropped to the top of the sulfate so that the sample can be loaded for subsequent chromatographic elution.

The elution sequence consists of 35 mL of hexane (Fraction 1), 30 mL of CH_2Cl_2 (Fraction 2), and 20 mL of 50:50 CH_2Cl_2 :methanol (Fraction 3). This sequence should yield primarily aliphatics and lower molecular weight aromatics and PNA's in Fraction 1; higher molecular weight aromatics and PNA's, halogenated compounds, and moderately polar substances in Fraction 2; and very polar substances in Fraction 3. In order to insure adequate resolution and reproducibility, the column elution rate should be maintained at 1 mL/min. The cooling water should be adjusted so as to maintain a constant temperature throughout the column.

The volume of solvents mentioned above represents volume added to the column for that fraction. If the volume of solvent collected is less than the volume actually added, due to evaporation, the fraction volume is restored to the proper level with fresh solvent. In all cases, the solvent level in the column is maintained at or above the top of the gel/sulfate bed; i.e., the sample-containing zone.

Each new solvent should be slowly added to the column to minimize disturbing the gel/sulfate bed and to eliminate trapped air bubbles, particularly in the zone of the sample-containing sodium sulfate.

From each fraction collected, nearly half is removed for a fractional GRAV analysis. The remainder is evaporated to 2 mL to be divided between TCO and GC/MS analyses. Figure C.7-10 is a facsimile of the LC fractionation QA/QC flow sheet used for each sample.

Sample No.: _____ Date: _____
 Silica Gel Lot No.: _____ CH_2Cl_2 Lot No.: _____
 Hexane Lot No.: _____ MeOH Lot No.: _____

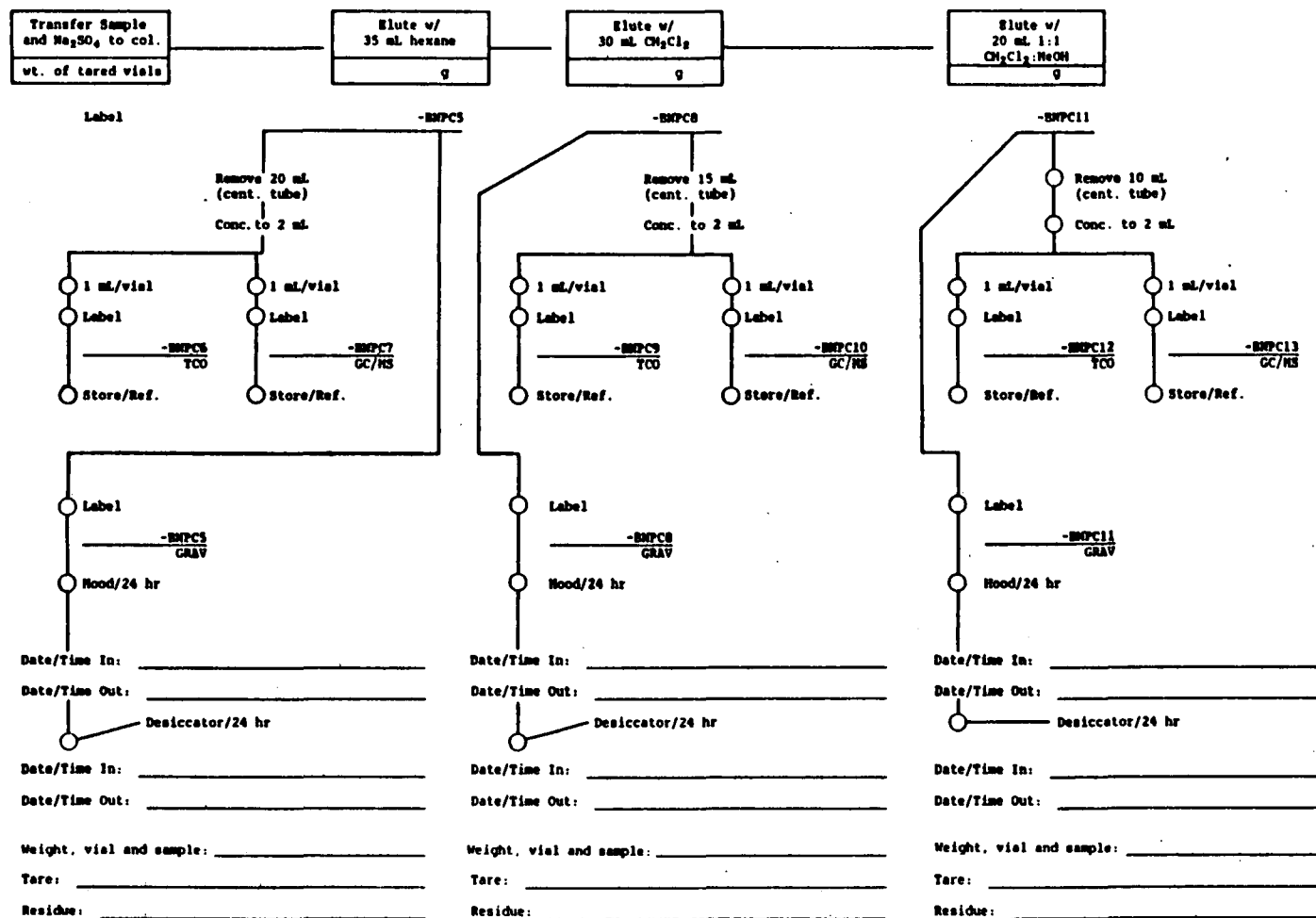


Figure C.7-10. Base/neutral flow sheet, LC fractionation.

C.8 EXTRACTABLE ORGANICS FROM SEDIMENTS

C.8.1 Extraction Procedure

The frozen sediment samples were fractured into suitably sized pieces for the freeze-drying containers, and were freeze dried in a Virtis freeze dryer at 0.01 mm Hg pressure. In certain samples, this process required in excess of 96 hours to complete, as the percentages of water in the samples were as high as 78.5%. The freeze-dried samples were homogenized and aliquots removed (coning/quartering method) for extraction. Another aliquot was removed for metals determination. The dried samples (approximately 30 g) were weighed into glass Soxhlet thimbles, equipped with sintered glass frits, and were each spiked with 1 mL CH_2Cl_2 solution containing 100.6 μg d_{10} -biphenyl; 101.0 μg d_{12} -chrysene; 107.6 μg d_4 -1,2-dichlorobenzene; 106.8 μg d_6 -phenol; 102.0 μg d_{12} -perylene; and 102.8 μg d_{10} -pyrene. These spiked samples were allowed to stand 0.5 hour to equilibrate. Each spiked sediment was extracted with 500 mL of methylene chloride for 24 hours. The organic extract was removed from the Soxhlet apparatus and was concentrated to ~5 mL in a rotary evaporator under water aspiration with a water bath temperature of ~35°C. The concentrated extracts were quantitatively transferred to a screw-cap vial with Teflon closure and the volume adjusted to ~10 mL. These concentrates were processed through a gel permeation chromatography (GPC) separation procedure.

The procedure used in processing sediments is diagrammed in Figure C.8-1.

C.8.2 GPC Cleanup Procedure

Methylene chloride extracts of sediment samples were fractionated to eliminate various compounds known to interfere with subsequent analytical measurements; i.e., fatty acids and molecular sulfur (S_8).

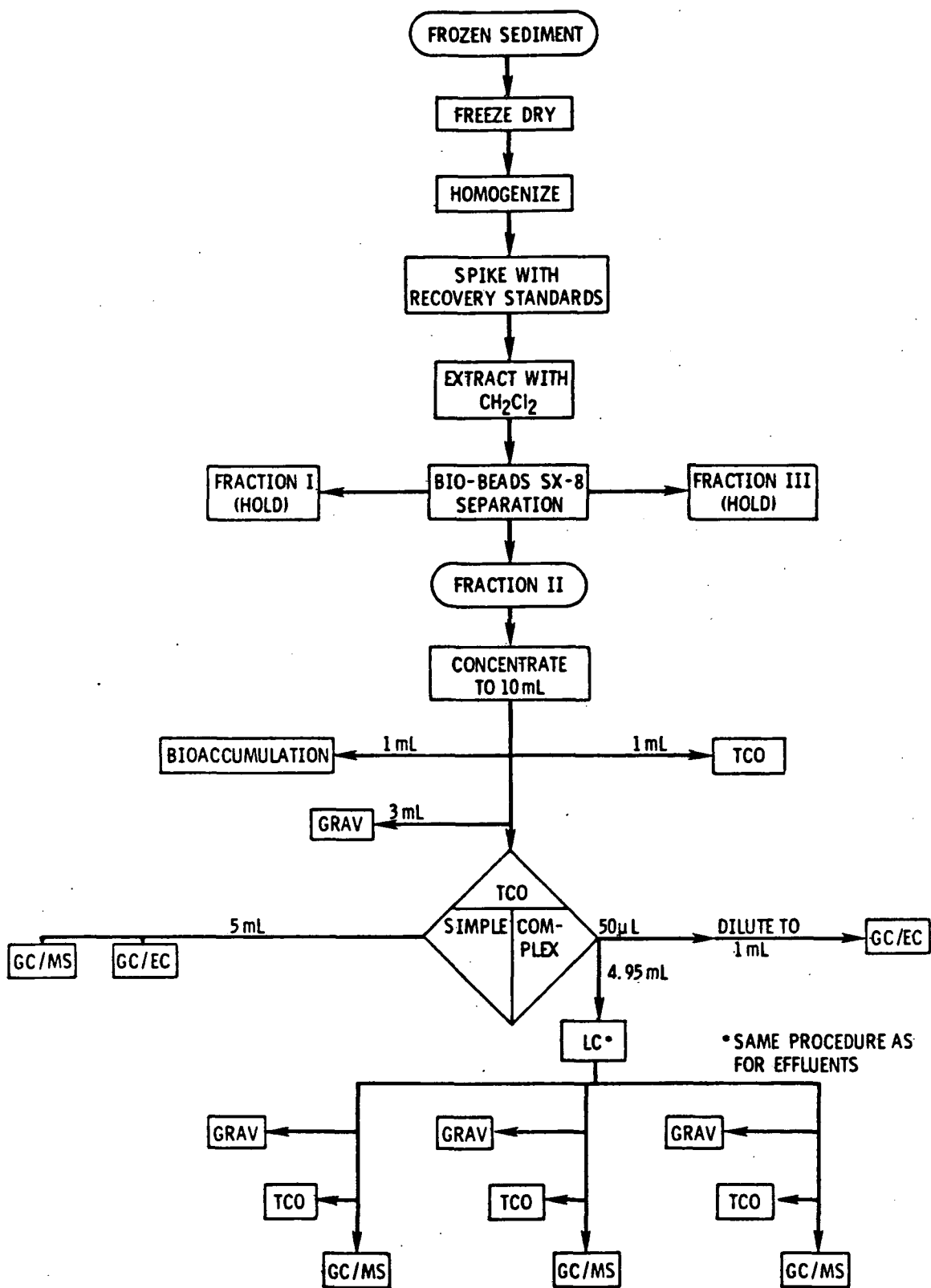


Figure C.8-1. Diagram of sediment processing and analysis scheme.

In Phase II, the chromatographic method employed to process the sediment extracts was based upon that developed by Stalling and co-workers [5]. The chromatographic support employed was Bio-Beads SX-3, manufactured and distributed by BioRad Laboratories, Richmond, California. When an eluent of 1:1 (V/V) cyclohexane/methylene chloride is employed, chlorinated pesticides, PCB's, dioxins, dibenzofurans, and all organic priority pollutants should elute over a reproducible volume. Fish oils, triglycerides, fatty acids, stearates, phthalates, and sulfur, which are commonly found in sediment extracts, should elute in other fractions (see Table C.8-1).

In Phase III, Bio-Beads SX-8@ was employed as the chromatographic support due to its increased separation capabilities for the polynuclear aromatic compounds (fraction two) and sulfur. 5.0 mL of a 10.0 mL extract was injected onto a 50 cm x 2.2 cm stainless steel column packed with 200/400 mesh Bio-Beads SX-8@ and eluted with 30% acetonitrile in methylene chloride (V/V) at 4.0 mL/min. The first fraction, 0-88 mL, and the third fraction, 256-~370 mL, were collected and archived. Fraction two, 88-256 mL, was collected, evaporated in a Kuderna-Danish concentrative evaporator to approximately 10-15 mL, and subsequently blown down with purified N₂ to less than 2-3 mL. At this point, some extracts precipitated in what appeared to be almost entirely acetonitrile. The fractions were easily redissolved with addition of methylene chloride to the original extract volume injected, 5.0 mL.

Figure C.8-2 is the UV chromatogram obtained at 254 nm when the standard spiking solution is fractionated according to the

-
- [5] Stalling, D. L., L. M. Smith, and J. D. Petty. Measurement of Organic Pollutants in Water and Wastewater. C. E. VanHall, ed., American Society for Testing and Materials, Philadelphia, Pennsylvania, 1979. pp. 302-323.

TABLE C.8-1. ELUTION VOLUMES OF VARIOUS COMPOUNDS
ON BIO-BEADS SX-3 2.0 cm x 100 cm WITH
1:1 (V/V) CYCLOHEXANE/METHYLENE CHLORIDE

Fish lipids	}	53 - 207 mL
Stearic Acid & β -Carotene		
DEHP		
DBP		
C ₁₂ -C ₂₄ Aliphatics		
Cholesterol		
Butylbenzene	}	207 - 373 mL
Chlorinated Pesticides		
Pentachloroanisole		
PCB's		
PCDF's		
PCDD's		
Hydroxy PCB's		
Toluene		
Biphenyl		
Acenaphthene		
Alkyl- and Chlorophenols		
Hexabromobiphenyl		
Anthracene		
Phenanthrene		
2,3-Benzofluorene		
Chloronaphthalenes		
Naphthalene and Fluorene		
2,4-D		
Pyrene		
Fluoranthene		
Benzo(a)pyrene		
Coronene		
4-Nitrophenol		
Sulfur		390 - 420 mL

previously described protocol. This chromatogram shows the excellent separation of the PNA's and sulfur. Figure C.8-3 shows a UV chromatogram at 254 nm obtained from a typical sediment extract. The value of this cleanup procedure is readily evident.

C.8-6

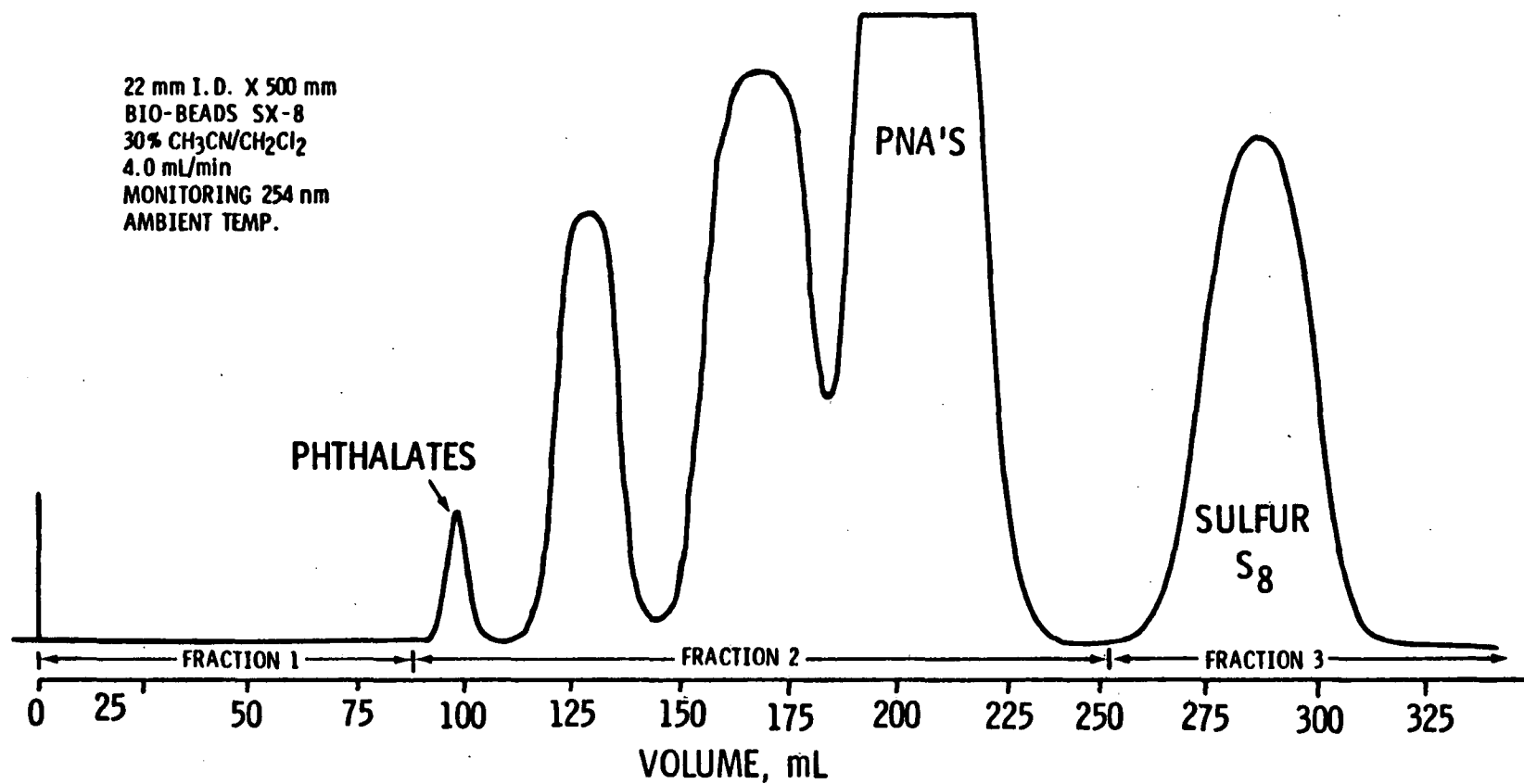


Figure C.8-2. Chromatogram of spiking standard.

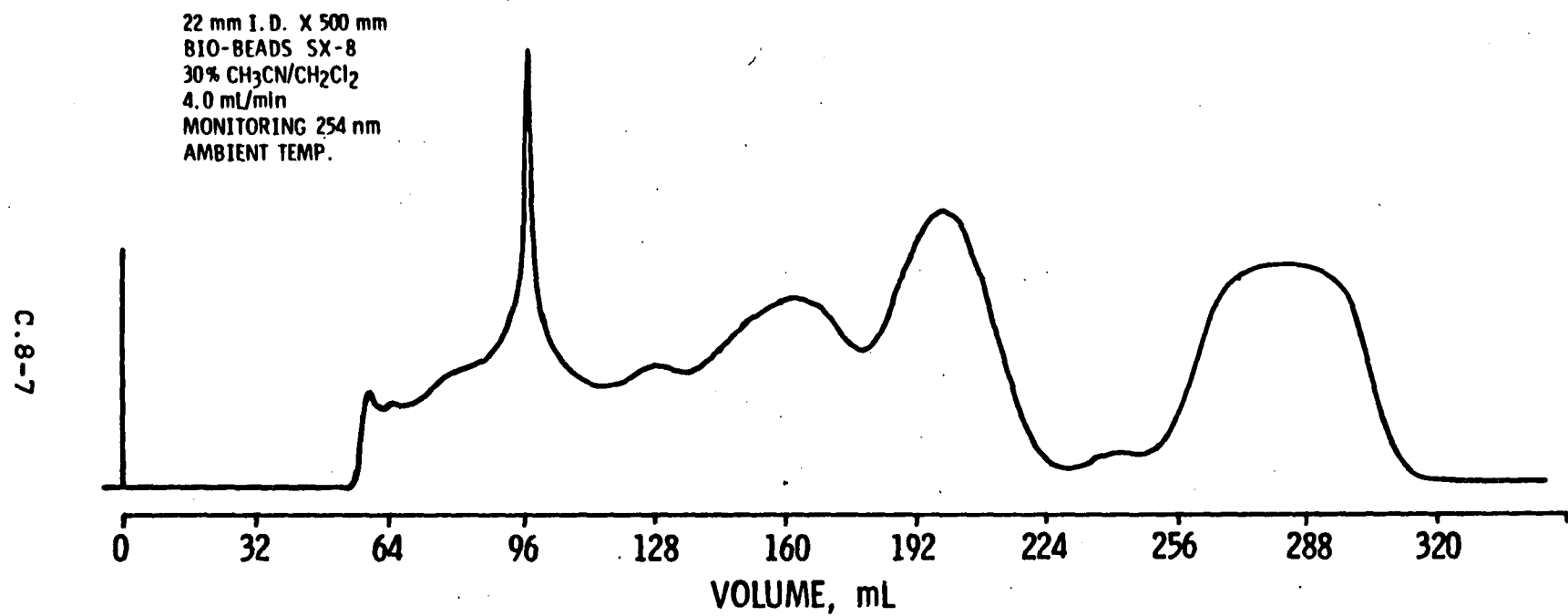


Figure C.8-3. Chromatogram of sample 8400.

C.9 ORGANIC CARBON TRACKING SYSTEM

C.9.1 Total Organic Carbon Procedure

The effluent samples were analyzed for total organic carbon following Procedure 505 given in Standard Methods [6]. The samples were acidified and sparged with CO₂-free nitrogen to remove inorganic carbon prior to analysis. The analysis was conducted via catalytic combustion to convert the organic to CO₂ followed by detection of the CO₂ with an infrared detector.

C.9.2 Total Chromatographable Organics (TCO) and Total Chromatographable Gravimetrics (TCG)

C.9.2.1 TCO/TCG Method--

An automated capillary GC/FID analysis was used to provide four types of information on the Phase III samples: total chromatographable organics (TCOs), total chromatographable gravimetrics (TCGs), relative retention indices, and recoveries of deuterated spike compounds.

The TCO analysis is a gas chromatographic procedure for quantitating materials boiling in the 100°C to 300°C range. The area of all peaks eluting between compounds having boiling points of 98°C and 302°C is integrated, and by comparison with standards, is reported as the TCO value in mg/L of original effluent water [7], or mg/g of sediment.

[6] Standard Methods for the Examination of Water and Wastewater, APHA, 14th Ed., Method 505, p. 532 (1975).

[7] U.S. Environmental Protection Agency, IERL-RTP Procedures Manual: Level I Environmental Assessment, 2nd ed., EPA-600/7-78-201, October 1978.

The end-points of the boiling range are defined by the retention times of n-heptane (C_7 , b.p. $98^{\circ}C$) and n-heptadecane (C_{17} , b.p. $302^{\circ}C$). Quantitation is based on standard solutions of known amounts of normal C_8 , C_{12} , and C_{16} hydrocarbons, with corrections made for solvent blanks and spiked deuterated compounds.

The TCG analysis was included in the Phase III protocol to determine what fraction of the GRAV organics can actually be chromatographed by capillary GC. For TCG, the areas of all peaks eluting between the retention times of n-heptadecane and the end of the FID chromatogram (51.00 min) are integrated. The boiling point range is from $300^{\circ}C$ to about $500^{\circ}C$. Quantitation is based on a standard composed of n- C_{20} and n- C_{24} alkanes, with corrections made for solvent blanks and spiked deuterated compounds. The results are reported in mg/L or original effluent water, or mg/g of sediment.

Figure C.9-1 depicts the division of a sample FID chromatogram into TCO and TCG regions.

The samples were analyzed using a Hewlett-Packard 5880 capillary column gas chromatograph with the following instrument conditions:

- 30 m fused silica column with SE-54 stationary phase
- linear flow velocity - 30 cm/s
- septum purge on at 0.5 min, at 100 mL/min
- initial temperature, $40^{\circ}C$
- held at initial temperature, 4 min
- then heated at a rate of $8^{\circ}C/min$
- with a final temperature of $280^{\circ}C$
- total analysis time, 51 min
- injector, splitless mode, temperature, $250^{\circ}C$
- FID temperature - $250^{\circ}C$
- Hewlett-Packard Model 3356 Laboratory Data System
- A/D acquisition rate, 8 samples/s
- injection volume, 1 μL

C.9-3

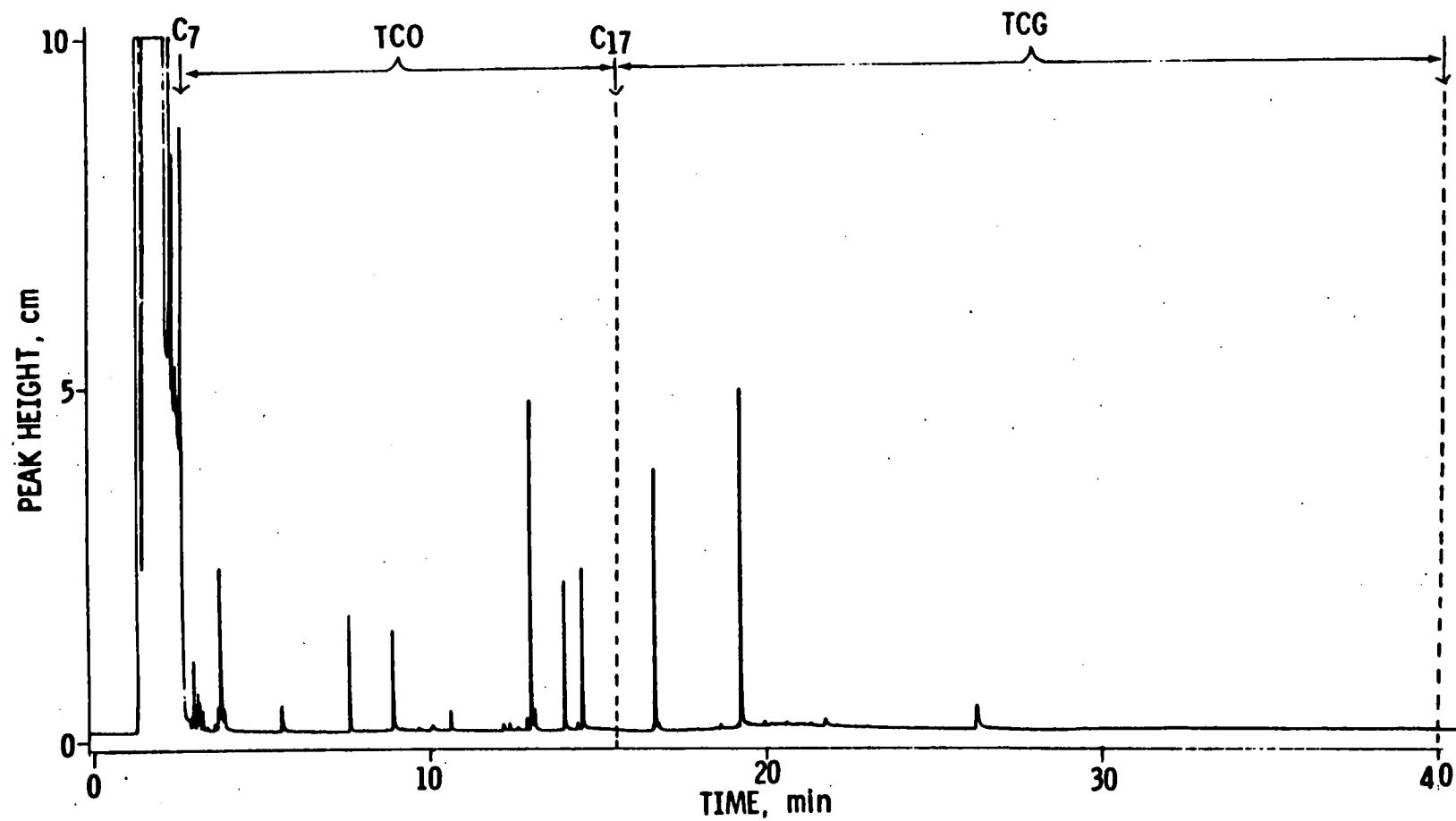


Figure C.9-1. Typical TCO/TCG trace on FID/GC.

Four types of standards were analyzed during the GC/FID determination of TCO's, TCG's, relative retention indices, and spike recoveries. Hydrocarbon standards containing C₈, C₁₂, C₁₆, C₂₀, and C₂₄ at 20, 100, or 250 µg/mL were analyzed to obtain FID response factors in the TCO and TCG ranges. A standard of C₇ and C₁₇ was used to determine the beginning (C₇) and end (C₁₇) of the TCO range of the chromatogram. A standard of six PNA retention time marker compounds was analyzed to calibrate the relative retention index segment of the analysis (see Section C.10), and standards of deuterated spike compounds were used to determine recoveries of spike compounds (see Section C.9.2.3). The numbers of each type of standard analyzed with each sample set are presented in Table C.9-1. The numbers of standards were adjusted for each set to be proportional to the number of samples. Retention time standards and hydrocarbon standards were run at the beginning and end of each analysis set to check for any variations in instrument parameters.

TABLE C.9-1. NUMBERS OF STANDARDS AND BLANKS ANALYZED WITH EACH GC/FID ANALYSIS SET FOR PHASE III

Analysis set	Spike recovery standards	Hydrocarbon standards	C ₇ & C ₁₇ retention time standards	PNA retention time standards	Methylene chloride blanks
Effluents	5	13	7	8	10
Effluent duplicates	2	4	2	2	3
Sediments	6	6	3	4	6
Sediment duplicates	3	4	2	2	3

C.9.2.2 Example TCO Calculation--

The following describes the calculation of a TCO value for the sediment sample, C169S: First, a raw TCO, in mg/mL, is obtained by computer data reduction of an FID run by summing all of the area integrated between the C₇ and C₁₇ retention time limits.

From this raw TCO is subtracted the average raw TCO for the solvent blank, as well as the concentrations of the spiking compounds eluting in the TCO range, as determined by GC/FID. (GC/MS concentrations are used when interferences prevent accurate GC/FID quantitation.) Finally, the appropriate factors are used to convert this corrected TCO value for the extract back to the TCO for the original sample.

For example, a raw TCO of 1.369 mg/mL was obtained for the sediment extract. From this was subtracted the background blank TCO of 0.002 mg/mL and the spike concentration of 0.133 mg/mL, to give a corrected TCO of 1.234 mg/mL. The corrected TCO was then converted from extract concentration to sample concentration as follows: Sample TCO (mg/g) = Corrected TCO ($\frac{\text{mg}}{\text{mL}}$) x final extract volume (mL)

$$\times \text{dilution factor at the instrument} \times \frac{10.0 \text{ mL initial extract}}{5.0 \text{ mL of initial extract fractionated by Bio-Beads}}$$

$$\times \frac{1}{\text{sample wt (g)}}$$

$$= 1.234 \frac{\text{mg}}{\text{mL}} \times 5.0 \text{ mL} \times \frac{10.0 \text{ mL}}{5.0 \text{ mL}}$$

$$\times \frac{1}{30.0 \text{ g}}$$

$$= 0.41 \mu\text{g/g of sediment}$$

C.9.2.3 QA/QC Results--

C.9.2.3.1. Reproducibility of TCO/TCG analyses--Duplicate analyses were performed for acid and base/neutral extracts of five plant effluent samples and for extracts of eleven sediment samples. The presented in Table C.9-2, while those of the sediments are presented in Table C.9-3. The duplicates were taken from separate

TABLE C.9.-2. TCO AND TCG RESULTS FROM DUPLICATE ANALYSES OF ACID AND BASE NEUTRAL FRACTIONS OF FIVE PLANT EFFLUENT SAMPLES

Plant No.	Plant No.	TCO-Acid fraction, mg/L			TCO-B/N fraction, mg/L			TCG-Acid fraction, mg/L			TCG-B/N fraction, mg/L		
		Run #1	Run #2	Avg	Run #1	Run #2	Avg	Run #1	Run #1	Avg	Run #1	Run #2	Avg
B112D	8219	0.99	0.93	0.96	2.59	2.41	2.50	0.88	1.04	0.96	1.68	1.77	1.72
B149S	8193	0.23	0.26	0.24	13.38	12.49	12.94	0.22	0.27	0.25	7.79	11.91	9.85
C150D	8237	0.61	0.69	0.65	0.45	0.35	0.40	0.48	0.61	0.54	0.55	0.49	0.52
C156D	8238	1.04	0.95	1.00	0.54	0.35	0.45	0.32	0.36	0.34	0.29	0.33	0.31
C161D	8239	0.89	0.66	0.78	1.57	1.03	1.30	1.29	1.07	1.18	2.26	2.16	2.21

TABLE C.9-3. TCO AND TCG RESULTS FROM DUPLICATE OR TRIPLICATE ANALYSES OF EXTRACTS OF ELEVEN PLANT SEDIMENT SAMPLES

Plant No.	Plant No.	TCO, mg/g				TCG, mg/g			
		Run #1	Run #2	Run #3	Avg ^a	Run #1	Run #2	Run #3	Avg
C161D	8377	0.01	0.01		0.01	0.24	0.30		0.27
C154D	8381	0.26	0.22	0.21	0.23	2.08	1.86	1.70	1.88
C153D	8382	0.04	0.04		0.04	0.31	0.32		0.32
B126S	8384	0.22	0.16	0.17	0.18	3.29	2.72	2.78	2.93
B141S	8385	0.21	0.18		0.20	1.26	1.10		1.18
B142S	8386	0.13	0.11		0.12	1.25	1.14		1.20
B143S	8387	1.75	1.73		1.74	3.25	4.09		3.67
C150D	8393	0.04	0.03		0.04	0.38	0.32		0.35
C169S	8396	0.41 ^b	0.40	0.42	0.41	3.56	3.65	3.27	3.49
B124D	8402	ND	ND	ND	ND	0.08	0.15	0.20	0.14
A101	8406	ND	ND	ND	ND	0.11	0.24	0.23	0.19

^aAvg = average.

^bND = less than 0.03 mg/g.

sample vials provided for TCO and GC/MS analyses, and were frequently of different dilutions. In order to isolate instrument variability from variations due to sample storage and dilution factors, several sediment samples were analyzed in triplicate. Referring to Table C.9-3, runs #2 and #3 were taken from the same vial, were at the same dilution, and were analyzed within four days of each other, while run #1 was analyzed at an earlier date, from a separate vial, and usually with less dilution. As expected, runs #2 and #3 generally provided better agreement.

C.9.2.3.2 Accuracy of TCO/TCG analyses--Measurement of recoveries of standards spiked into a sample and then carried through the workup scheme is a very useful tool for gauging the accuracy of an analysis in terms of the actual percentage of sample that is quantified at the instrument. Since all samples were not analyzed by GC/MS for Phase III, the decision was made to measure recoveries of six deuterated spikes by GC/FID. While there are some problems with interferences when measuring spike concentrations using a nonspecific detector such as an FID, this measurement provides a feel for the quantity of material making it through the sample work-up procedure, and provides a quite accurate measurement when samples are relatively clean. The good agreement between the GC/MS and GC/FID recovery data attests to the value of the FID.

Recoveries of the acid spike (phenol-d₅) in the acid extract of the plant effluents can be found in Table C.9-4, while recoveries of base/neutral spikes (1,2-dichlorobenzene-d₄, biphenyl-d₁₀, pyrene-d₁₂, chrysene-d₁₂, and perylene-d₁₂) in the base/neutral extract can be found in Table C.9-5. Recoveries of all deuterated spikes in the sediment extracts are presented in Table C.9-6.

Where samples were analyzed in duplicate or triplicate, spike recoveries were calculated in duplicate or triplicate, also.

TABLE C.9-4. RECOVERIES OF DEUTERATED SPIKE COMPOUND (PHENOL-D₅) IN ACID FRACTIONS OF PLANT EFFLUENT SAMPLES, AS DETERMINED BY GC/FID

		Effluent No./Plant No.									
		8182					8186				
		Method	8183	8184	8185	Reagent	8188	8191	8192	8193	8194
		Blank	B133S	B142S	B141S	Blank	B143S	B126S	B147S	B149S	C169S
Phenol-D ₅											
Conc. spiked, µg/L	223.0										
Conc. found, µg/L	55.0	55.7	ND ^a	54.9	130	82.5	48.7	48.8	42.2 ^b	68.2	
% Recovery	24.7	25.0	0	24.6	58.2	37.0	21.8	21.9	18.9 ^b	30.6	
		8204	8205	8206	8207	8208	8209	8210	8211	8212	8217
		B113D	B119D	B124D	B111D	C169D	C151D	C158D	C157D	C164D	A101C
Phenol-D ₅											
Conc. spiked, µg/L							446.0 ^d	223.0	223.0		
Conc. found, µg/L	45.8	- ^c	53.9	54.4	50.0	57.8	37.3	51.9	59.0	55.1	
% Recovery	20.6	- ^c	24.2	24.4	22.4	13.0	16.7	23.3	26.4	24.7	
		8218	8219	8225	8230	8233	8237	8238	8239	8240	8245
		C160D	B112D	C153D	C155D	A109	C150D	C156D	C161D	C154D	C159D
Phenol-D ₅											
Conc. spiked, µg/L							200.6 ^b				
Conc. found, µg/L	54.1	59.4 ^b	59.9	66.6	46.6	42.8 ^b	69.7 ^b	72.2 ^b	59.4	54.8	
% Recovery	24.3	26.6 ^b	26.9	30.0	20.9	21.3 ^b	34.7 ^b	36.0 ^b	26.6	27.3	

^a Not detected.

^b Average of duplicate analyses.

^c Could not be quantitated by FID because co-eluting interference was present.

^d Spike concentration double because sample volume was only 5 L.

TABLE C.9-5. RECOVERIES OF DEUTERATED SPIKE COMPOUNDS IN BASE/NEUTRAL FRACTIONS OF PLANT EFFLUENT SAMPLES AS DETERMINED BY GC/FID

		Effluent No./Plant No.														
		8182	8186													
		Method	8183	8184	8185	Reagent	8188	8191	8192	8193	8194	8204	8205	8206	8207	8208
		blank	B133S	B142S	B141S	blank	B143S	B126S	B147S	B149S	C169S	B113D	B119D	B124D	B111D	C169D
Phenol-D ₅																
Conc. spiked, µg/L		223.0														
Conc. found, µg/L		ND ^a	12.1	18.9	ND	25.4	ND	ND	ND	ND	5.3	ND	ND	ND	ND	ND
% Recovery		0	5.4	8.5	0	11.3	0	0	0	0	2.4	0	0	0	0	0
1,2-Dichlorobenzene-D- ₄																
Conc. spiked, µg/L		118.1														
Conc. found, µg/L		92.1	76.4	75.1	130	108	78.5	87.9	88.3	81.4 ^b	64.5	80.6	58.6	65.6	53.5	81.1
% Recovery		80.0	64.7	63.6	110	91.8	66.5	74.4	74.8	68.9 ^b	54.6	68.2	49.6	55.5	45.3	68.7
Biphenyl-D ₁₀																
Conc. spiked, µg/L		101.6														
Conc. found, µg/L		89.3	87.4	76.8	105	105	90.6	87.4	92.4	85.9 ^b	59.3	88.8	67.4	72.0	62.3	88.8
% Recovery		87.9	86.1	75.5	103	104	89.1	86.0	90.9	84.6 ^b	58.3	87.4	66.4	70.8	61.3	87.4
Pyrene-D ₁₂																
Conc. spiked, µg/L		99.3														93.1
Conc. found, µg/L		97.1	85.4	68.0	- ^c	106	61.9	74.8	63.6	50.6 ^b	43.0	69.9	59.4	54.8	49.9	59.4
% Recovery		97.8	86.0	68.5	- ^c	107	62.3	75.4	64.1	50.9 ^b	43.3	70.4	59.8	55.2	50.2	63.8
Chrysene-D ₁₂																
Conc. spiked, µg/L		83.0	8.5					83.0								78.8
Conc. found, µg/L		74.2	9.0	6.5	6.1	10.4	5.6	68.0	81.1	46.8 ^b	24.7	77.1	64.3	60.6	52.9	60.4
% Recovery		89.4	106	77	72	123	65	81.9	97.8	56.4 ^b	29.8	92.9	77.5	73.0	63.7	72.7
Perylene-D ₁₂																
Conc. spiked, µg/L		85.0	100.0					85.0								
Conc. found, µg/L		37.3	81.5	56.9	45.2	88.0	80.6	62.6	111	25.9 ^e	18.2	89.1	62.3	60.5	49.5	54.7
% Recovery		43.9	81.5	56.9	45.2	88.0	80.6	73.7	131	28.6 ^e	21.5	105	73.3	71.2	58.2	64.3

(continued)

TABLE C.9-5 (continued)

	Effluent No./Plant No.														
	8209 C151D	8210 C158D	8211 C157D	8212 C164D	8217 A101	8218 C160D	8219 B112D	8225 C153D	8230 C155D	8233 A109	8237 C150D	8238 C156D	8239 C161D	8240 C154D	8245 C159D
Phenol-D ₅															
Conc. spiked, µg/L	446.0 ^d	223.0	223.0								200.6				
Conc. found, µg/L	ND	ND	ND	ND	ND	ND	ND ^b	ND	5.7	ND	ND ^b	2.0 ^b	8.2 ^b	ND	ND
% Recovery	0	0	0	0	0	0	0 ^b	0	2.5	0	0 ^b	1.0 ^b	4.0 ^b	0	0
1,2-Dichlorobenzene-D ₄															
Conc. spiked, µg/L	236.2 ^d	118.1	118.1												
Conc. found, µg/L	172.8	63.6	80.1	68.1	79.0	76.1	79.6 ^b	74.9	86.8	59.5	69.4 ^b	106 ^b	148 ^b	83.5	82.7
% Recovery	73.2	53.9	67.8	57.7	66.9	64.5	67.4 ^b	63.4	73.5	50.4	58.8 ^b	89.7 ^b	126 ^b	70.7	70.0
Biphenyl-D ₁₀															
Conc. spiked, µg/L	203.2 ^d	101.6	101.6												
Conc. found, µg/L	162.4	63.4	78.4	66.2	80.4	77.3	107 ^b	73.9	84.3	65.1	52.4 ^b	38.0 ^b	102 ^b	78.9	77.0
% Recovery	80.0	62.4	77.1	65.2	79.2	76.1	106 ^b	72.8	82.9	64.1	51.5 ^b	37.4 ^b	101 ^b	77.6	75.8
Pyrene-D ₁₂															
Conc. spiked, µg/L	198.6 ^d	99.3	99.3												
Conc. found, µg/L	162.8	64.5	74.2	56.3	74.4	73.8	49.6 ^b	72.7	47.8	39.3	35.3 ^b	26.4 ^b	56.2 ^b	82.4	69.8
% Recovery	82.0	65.0	74.7	56.7	74.9	74.4	50.0 ^b	73.2	48.1	39.6	35.6 ^b	26.5 ^b	56.6 ^b	83.0	70.3
Chrysene-D ₁₂															
Conc. spiked, µg/L	171.6 ^d	85.8	85.8												
Conc. found, µg/L	162.0	75.6	69.1	62.8	70.1	53.8	53.8 ^b	46.3	49.1	33.8	31.4 ^b	22.4 ^b	56.5 ^b	55.3	66.5
% Recovery	94.4	88.1	80.5	73.2	81.7	62.7	62.6 ^b	53.9	57.2	39.5	36.6 ^b	26.2 ^b	65.8 ^b	64.5	77.5
Perylene-D ₁₂															
Conc. spiked, µg/L	181.2 ^d	90.6	90.6												
Conc. found, µg/L	150.0	88.4	73.1	82.0	75.7	54.2	46.0 ^b	25.8	75.5	38.6	35.1 ^b	24.0 ^b	44.5 ^b	39.5	72.5
% Recovery	82.8	97.6	80.7	90.6	83.5	59.9	50.8 ^b	28.5	83.3	42.6	38.8 ^b	26.5 ^b	49.1 ^b	43.6	80.0

^aNot detected.^bAverage of duplicate analyses.^cLarge interfering peak prevented determination by GC/FID.^dSpike concentration double because sample volume was only 5 L.^eValues for perylene were obtained from a third analysis of this sample, in which no dilution was made. Poor peak shape for perylene in this extremely dirty sample prohibited accurate quantitation in the first two analyses, in which the sample was diluted 1:10.

TABLE C.9-6. RECOVERIES OF DEUTERATED SPIKE COMPOUNDS IN ANALYSES OF EXTRACTS OF SEDIMENT SAMPLES, AS DETERMINED BY GC/FID

	Sediment No./Plant No.											
	8377 C161D	8379 C156D	8380 B112D	8381 C154D	8382 C153D	8383 C159D	8384 B126S	8385 B141S	8386 B142S	8387 B143S	8393 C150D	8394 C158D
Phenol-D ₈												
Conc. spiked, µg/L	35.6											
Conc. found, µg/L	11.9 ^a	24.0	53.5	9.0 ^b	1.6 ^a	30.8	19.9 ^b	5.9 ^a	20.8 ^a	24.7 ^a	12.0 ^a	25.0
% Recovery	33.4 ^a	67.4	150	25.4 ^b	4.4 ^a	86.5	53.2 ^b	16.6 ^a	58.3 ^a	69.4 ^a	33.6 ^a	70.2
1,2-Dichlorobenzene-D ₄												
Conc. spiked, µg/L	35.9											
Conc. found, µg/L	9.2 ^a	16.8	25.0	3.7 ^b	20.6 ^a	21.1	15.3 ^b	18.1 ^a	15.4 ^a	19.7 ^a	4.0 ^a	18.4
% Recovery	25.6 ^a	46.8	70.0	102 ^b	57.4 ^a	58.8	45.3 ^b	50.4	42.7 ^a	54.9 ^a	11.2 ^a	51.3
Biphenyl-D ₁₀												
Conc. spiked, µg/L	33.5											
Conc. found, µg/L	14.5 ^a	24.6	- ^c	24.2 ^a	26.4 ^a	34.0	22.7 ^b	28.8 ^a	23.0 ^a	28.7 ^a	23.4 ^a	26.9
% Recovery	43.3 ^a	73.4	- ^c	72.2 ^b	78.8 ^a	101	67.8 ^b	86.0 ^a	68.7 ^a	85.7 ^a	69.9 ^a	80.3
Pyrene-D ₁₂												
Conc. spiked, µg/L	34.3											
Conc. found, µg/L	20.1 ^a	34.6	- ^c	24.2 ^a	27.4 ^a	33.1	22.5 ^b	22.1 ^a	24.0 ^a	26.0 ^a	21.3 ^a	25.6
% Recovery	58.6 ^a	101	- ^c	70.7 ^a	80.0 ^a	96.5	65.7 ^b	64.4 ^a	70.1 ^a	75.7 ^a	62.1 ^a	74.6
Chrysene-D ₁₂												
Conc. spiked, µg/L	33.7											
Conc. found, µg/L	25.0 ^a	42.6	- ^c	32.4 ^a	36.8 ^a	38.6	29.4 ^b	32.4 ^a	35.0 ^a	34.1 ^a	25.8 ^a	28.3
% Recovery	74.0 ^a	126	- ^c	96.1 ^a	110 ^a	115	87.2 ^b	95.4 ^a	104 ^a	101 ^a	76.6 ^a	84.0
Perylene-D ₁₂												
Conc. spiked, µg/L	34.0											
Conc. found, µg/L	27.7 ^a	52.0	- ^c	28.0 ^a	30.6 ^a	32.9	29.4 ^b	38.2 ^a	33.8 ^a	32.8 ^a	28.0 ^a	30.4
% Recovery	81.5 ^a	153	- ^c	82.5 ^a	89.8 ^a	96.8	86.6 ^b	112 ^a	99.4 ^a	96.3 ^a	82.8 ^a	89.4

(continued)

TABLE C.9-6 (continued)

	Sediment No./Plant No.										8420 Spiked water
	8395 C151D	8396 C169S	8400 A109	8401 B113D	8402 B124D	8403 C157D	8404 B119D	8405 C160D	8406 A101	8407 C164D	
Phenol-D ₅											
Conc. spiked, µg/g				35.6							
Conc. found, µg/g	17.5	7.5 ^b	24.1	25.8	25.5 ^b	22.7	25.0	22.1	24.6 ^b	28.6	ND
% Recovery	49.2	21.0 ^b	67.7	72.5	71.7 ^b	63.8	70.2	62.1	69.2 ^b	80.3	0
1,2-Dichlorobenzene-D ₄											
Conc. spiked, µg/g				35.9							
Conc. found, µg/g	10.0	3.9 ^b	17.2	17.0	17.0 ^b	17.1	19.7	15.5	14.6 ^b	19.7	ND
% Recovery	27.9	10.8 ^b	47.9	47.4	47.3 ^b	47.6	54.9	43.2	40.8 ^b	54.9	0
Biphenyl-D ₁₀											
Conc. spiked, µg/g				33.5							
Conc. found, µg/g	24.6	24.5 ^b	25.4	28.8	27.1 ^b	24.9	29.1	25.4	27.4 ^b	30.0	ND
% Recovery	73.4	73.1 ^b	75.8	86.0	80.9 ^b	74.3	86.9	75.8	81.9	89.6	0
Pyrene-D ₁₂											
Conc. spiked, µg/g				34.3							
Conc. found, µg/g	25.1	22.2 ^b	20.0	24.9	26.4 ^b	22.8	25.9	22.3	24.9 ^b	27.0	3.7
% Recovery	73.2	54.7 ^b	58.3	72.6	76.5 ^b	66.5	75.5	65.0	72.6 ^b	78.7	10.8
Chrysene-D ₁₂											
Conc. spiked, µg/g				33.7							
Conc. found, µg/g	27.8	32.3 ^b	21.2	26.6	31.4 ^b	25.4	29.6	25.1	29.5 ^b	31.4	31.1
% Recovery	82.6	95.9 ^b	62.9	78.9	73.2 ^b	78.3	87.8	74.5	87.7 ^b	93.2	92.3
Perylene-D ₁₂											
Conc. spiked, µg/g				34.0							
Conc. found, µg/g	26.0	27.2 ^b	23.2	32.2	31.3 ^b	31.6	32.5	30.6	29.5 ^b	36.7	35.3
% Recovery	76.5	79.9 ^b	68.2	94.7	92.2 ^b	92.9	95.6	90.0	86.9 ^b	108	104

^a Average of duplicate analyses.^b Average of triplicate analyses.^c Could not be quantitated by GC/FID because interference(s) present.

Tables C.9-7, C.9-8, and C.9-9 provide results of duplicate (or triplicate) recovery determinations for acid extracts of effluents, base/neutral extracts of effluents, and sediment extracts, respectively.

In general, the recovery tables indicate that there is some sample-to-sample variability in the extraction efficiency of organic compounds, probably due primarily to matrix effects. None of the GC/FID or GC/MS data have been corrected for recovery, but the reader should be aware that the actual levels of organics in the samples are probably higher than those stated in the tables, especially for the sediment samples. The sediment spiking (Table C.9-6) was performed after freeze-drying, a process in which large quantities of semivolatile compounds may be lost. The recoveries of deuterated spikes from a water sample spiked prior to freeze-drying (sample 8420-spiked water) demonstrate this phenomenon.

C.9.3 GRAV Analysis

Gravimetric analyses were used for quantitative determination of the mass of organics with boiling points in excess of 300°C. In the case of the effluents, 4 mL aliquots of the concentrated extracts were evaporated to dryness in a hood and then desiccated over Drierite® for 24 hours and weighed to constant weight (± 0.1 mg). For sediments, 3 mL of the GPC fraction II concentrate was used for the GRAV determination. The evaporated residue weights were then used to calculate the GRAV results in terms of mg/L of original effluent sample and $\mu\text{g/g}$ lyophilized sediment.

TABLE C.9-7. DEUTERATED SPIKE RECOVERIES RESULTING FROM DUPLICATE GC/FID ANALYSES OF ACID FRACTIONS OF FIVE PLANT EFFLUENT

	Effluent No./Plant No.								
	8193 B149S	8193 Dup B149S	8193 Avg B149S	8219 B112D	8219 Dup B112D	8219 Avg B112D	8237 C150D	8237 Dup C150D	8237 Avg C150D
Phenol-D ₅									
Conc. spiked, µg/L	223.0						200.6		
Conc. found, µg/L	35.0	49.4	42.2	53.4	65.4	59.4	33.5	52.0	42.8
% Recovery	15.7	22.1	18.9	23.9	29.3	26.6	16.7	25.9	21.3
	8238 C156D	8238 Dup C156D	8238 Avg C156D	8239 C161D	8239 Dup C161D	8239 Avg C161D			
Phenol-D ₅									
Conc. spiked, µg/L									
Conc. found, µg/L	69.7	82.7	76.2	72.2	66.5	69.4			
% Recovery	34.7	41.3	38.0	36.0	33.2	34.6			

C.9-14

TABLE C.9-8. DEUTERATED SPIKE RECOVERIES RESULTING FROM DUPLICATE GC/FID ANALYSES OF BASE/NEUTRAL FRACTIONS OF FIVE PLANT EFFLUENT SAMPLES

	Effluent No./Plant No.														
	8193	8193		8219	8219		8237	8237		8238	8238		8239	8239	
	8193	Dup	Avg	8219	Dup	Avg	8237	Dup	Avg	8238	Dup	Avg	8239	Dup	Avg
	B149S	B149S	B149S	B112D	B112D	B112D	C150D	C150D	C150D	C156D	C156D	C156D	C161D	C161D	C161D
Phenol-D ₈															
Conc. spiked, µg/L	223.0						200.6								
Conc. found, µg/L	ND ^a	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.0	2.0	6.7	9.6	8.2
% Recovery	0	0	0	0	0	0	0	0	0	0	2.0	1.0	3.3	4.8	4.0
1,2-Dichlorobenzene-D ₄															
Conc. spiked, µg/L	118.1														
Conc. found, µg/L	77.3	85.5	81.4	64.3	94.8	79.6	61.9	76.9	69.4	94.8	117	106	142	155	148
% Recovery	65.4	72.4	68.9	54.5	80.2	67.4	52.4	65.1	58.8	80.3	99.1	89.7	120	131	126
Biphenyl-D ₁₀															
Conc. spiked, µg/L	101.6														
Conc. found, µg/L	79.9	91.9	85.9	87.7	127	107	50.1	54.6	52.4	37.2	38.7	38.0	99.2	106	102
% Recovery	78.7	90.4	84.6	86.4	125	106	49.3	53.7	51.5	36.6	38.1	37.4	97.6	105	101
Pyrene-D ₁₂															
Conc. spiked, µg/L	99.3														
Conc. found, µg/L	46.9	54.3	50.6	49.6	49.7	49.6	34.5	36.1	35.3	24.6	28.1	26.4	51.9	60.6	56.2
% Recovery	47.2	54.6	50.9	50.0	50.0	50.0	34.8	36.4	35.6	24.7	28.3	26.5	52.2	61.0	56.6
Chrysene-D ₁₂															
Conc. spiked, µg/L	83.0			85.8											
Conc. found, µg/L	46.3	47.4	46.8	43.5	64.1	53.8	31.6	31.2	31.4	21.4	23.5	22.4	53.2	59.8	56.5
% Recovery	55.8	57.1	56.4	50.6	74.7	62.6	36.9	36.4	36.6	24.9	24.7	26.2	62.0	69.7	65.8
Perylene-D ₁₂															
Conc. spiked, µg/L	85.0			90.6											
Conc. found, µg/L	0 ^b ND	0 ^b ND	0 ^b ND	41.8	50.3	46.0	37.2	33.0	35.1	24.5	23.5	24.0	42.8	46.2	44.5
% Recovery	0 ^b	0 ^b	0 ^b	46.1	55.6	50.8	41.1	36.4	38.8	27.1	25.9	26.5	47.2	51.0	49.1

^aNot detected.

^bSince this sample exhibited a high level of organics, it was diluted 1:10 for the duplicate analyses, which resulted in the perylene-d₁₂ spike being below the detection limit. The sample was analyzed a third time without dilution, and perylene-d₁₂ was found at 25.9 µg/L, or 28.6% recovery.

TABLE C.9-9. DEUTERATED SPIKE RECOVERIES RESULTING FROM DUPLICATE OR TRIPPLICATE GC/FID ANALYSES OF EXTRACTS OF ELEVEN PLANT SEDIMENT SAMPLES

	Sediment 8377 Plant C161D			Sediment 8381 Plant C154D				Sediment 8382 Plant C153D			Sediment 8384 Plant B126S			
	Run #1	Run #2	Avg ^a	Run #1	Run #2	Run #3	Avg	Run #1	Run #2	Avg	Run #1	Run #2	Run #3	Avg
Phenol-D ₅														
Conc. spiked, µg/g	35.6													
Conc. found, µg/g	12.0	11.8	11.9	10.6	8.7	7.8	9.0	1.5	1.6	1.6	22.7	18.0	16.1	19.9
% Recovery	33.7	33.1	33.4	29.8	24.4	21.9	25.4	4.2	4.5	4.4	63.8	50.6	45.2	53.2
1,2-Dichlorobenzene-D ₄														
Conc. spiked, µg/g	35.9													
Conc. found, µg/g	9.3	9.1	9.2	3.9	3.6	3.5	3.7	20.6	20.7	20.6	16.8	16.8	15.2	15.3
% Recovery	25.9	25.3	25.6	10.9	10.0	9.7	10.2	57.4	57.7	57.4	46.8	46.8	42.3	45.3
Biphenyl-D ₁₀														
Conc. spiked, µg/g	33.5													
Conc. found, µg/g	14.7	14.3	14.5	26.6	23.8	22.2	24.2	26.2	26.5	26.4	25.6	22.4	20.1	22.7
% Recovery	43.9	42.7	43.3	79.4	71.0	66.3	72.2	78.2	79.1	78.8	76.4	66.9	60.0	67.8
Pyrene-D ₁₂														
Conc. spiked, µg/g	34.3													
Conc. found, µg/g	19.8	20.4	20.1	- ^b	25.8	22.7	24.2	23.9	31.0	27.4	26.4	20.8	20.4	22.5
% Recovery	57.7	59.5	58.6	- ^b	75.2	66.2	70.7	69.7	90.4	80.0	77.0	60.6	59.5	65.7
Chrysene-D ₁₂														
Conc. spiked, µg/g	33.7													
Conc. found, µg/g	22.7	27.2	25.0	- ^b	33.9	30.9	32.4	29.2	44.3	36.8	37.4	26.2	24.6	29.4
% Recovery	67.4	80.7	74.0	- ^b	100.6	91.7	96.1	86.6	131	110	111	77.7	73.0	87.2
Perylene-D ₁₂														
Conc. spiked, µg/g	34.0													
Conc. found, µg/g	30.9	24.5	27.7	- ^b	29.4	26.7	28.0	31.9	29.2	30.6	41.9	24.3	22.1	29.4
% Recovery	90.9	72.1	81.5	- ^b	85.6	78.5	82.5	93.8	85.8	89.8	123	71.5	65.0	86.6

(continued)

TABLE C.9-9 (continued)

	Sediment 8385 Plant B141S			Sediment 8386 Plant B142S			Sediment 8387 Plant B143S			Sediment 8393 Plant C150D		
	Run #1	Run #2	Avg	Run #1	Run #2	Avg	Run #1	Run #2	Avg	Run #1	Run #2	Avg
Phenol-D₈												
Conc. spiked, µg/g	35.6											
Conc. found, µg/g	5.8	6.0	5.9	23.0	18.5	20.8	27.9	21.5	24.7	12.0	11.9	12.0
% Recovery	16.3	16.9	16.6	64.6	52.0	58.3	78.4	60.4	69.4	33.7	33.4	33.6
1,2-Dichlorobenzene-D₄												
Conc. spiked, µg/g	35.9											
Conc. found, µg/g	17.3	18.9	18.1	15.7	15.0	15.4	19.4	20.0	19.7	4.0	4.1	4.0
% Recovery	48.2	52.6	50.4	43.7	41.8	42.7	54.0	55.7	54.9	11.1	11.4	11.2
Biphenyl-D₁₀												
Conc. spiked, µg/g	33.5											
Conc. found, µg/g	28.5	29.1	28.8	25.8	20.2	23.0	31.3	26.1	28.7	23.7	23.2	23.4
% Recovery	85.1	86.9	86.0	77.0	60.3	68.7	93.4	77.9	85.7	70.7	69.3	69.9
Pyrene-D₁₂												
Conc. spiked, µg/g	34.3											
Conc. found, µg/g	21.2	23.1	22.1	24.5	23.6	24.0	22.3	29.6	26.0	21.5	21.1	21.3
% Recovery	61.8	67.3	64.4	71.4	68.8	70.1	65.0	86.3	75.7	62.7	61.5	62.1
Chrysene-D₁₂												
Conc. spiked, µg/g	33.7											
Conc. found, µg/g	30.8	34.1	32.4	34.0	36.1	35.0	35.1	33.1	34.1	25.9	25.7	25.8
% Recovery	91.4	101	95.4	101	107	104	104	98.2	101	76.9	76.3	76.6
Perylene-D₁₂												
Conc. spiked, µg/g	34.0											
Conc. found, µg/g	42.3	34.2	38.2	41.8	25.8	33.8	43.4	22.1	32.8	30.2	25.7	28.0
% Recovery	124	101	112	123	75.9	99.4	128	65.0	96.3	88.8	75.6	82.2

(continued)

TABLE C.9-9 (continued)

	Sediment 8396 Plant C169S				Sediment 8402 Plant B124D				Sediment 8406 Plant A101			
	Run #1	Run #2	Run #3	Avg	Run #1	Run #2	Run #3	Avg	Run #1	Run #2	Run #3	Avg
Phenol-D ₅												
Conc. spiked, µg/g	35.6											
Conc. found, µg/g	10.2	6.3	5.9	7.5	25.4	26.1	25.1	25.5	25.7	25.0	23.2	24.6
% Recovery	28.7	17.7	16.6	21.0	71.3	73.3	70.5	71.7	72.2	70.2	65.2	69.2
1,2-Dichlorobenzene-D ₄												
Conc. spiked, µg/g	35.9											
Conc. found, µg/g	4.6	3.6	3.5	3.9	16.7	17.4	16.8	17.0	14.9	14.9	14.1	14.6
% Recovery	12.8	10.0	9.7	10.8	46.5	48.5	46.8	47.3	41.5	41.5	39.3	40.8
Biphenyl-D ₁₀												
Conc. spiked, µg/g	33.5											
Conc. found, µg/g	29.5	22.1	21.8	24.5	28.4	26.9	26.0	27.1	29.8	27.4	25.1	27.4
% Recovery	88.1	66.0	65.1	73.1	84.8	80.3	77.6	80.9	89.0	81.8	74.9	81.9
Perylene-D ₁₂												
Conc. spiked, µg/g	34.3											
Conc. found, µg/g	25.0	20.7	20.9	22.2	24.6	27.6	27.1	26.4	25.1	25.7	23.9	24.9
% Recovery	72.9	60.3	60.9	64.7	70.0	80.5	79.0	76.5	73.2	74.9	69.7	72.6
Chrysene-D ₁₂												
Conc. spiked, µg/g	33.7											
Conc. found, µg/g	37.9	32.7	26.4	32.3	28.2	33.1	32.9	31.4	28.6	31.2	28.8	29.5
% Recovery	112	97.0	78.3	95.9	83.7	98.2	97.6	93.2	84.9	92.6	85.5	87.7
Perylene-D ₁₂												
Conc. spiked, µg/g	34.0											
Conc. found, µg/g	25.5	28.9	27.1	27.2	35.0	30.0	29.0	31.3	35.0	28.5	25.1	29.5
% Recovery	75.0	85.0	79.7	79.9	103	88.2	85.3	92.2	103	83.8	73.8	86.9

^a Average.^b Could not be quantitated when undiluted sample was analyzed because column overloading resulted in peaks for spike compounds being poorly resolved from interferences.

C.10 RELATIVE RETENTION INDICES

Relative retention indices for peaks eluting within the GC/FID and GC/MS chromatograms were determined in order to compare the data obtained during the TCO/TCG analyses with GC/MS data and chromatographic data generated at the Virginia Institute of Marine Sciences Laboratories by R. J. Huggett. This approach shows the feasibility of a preliminary identification of components present in a given extract, based upon this index. A standard mixture of PNAs was prepared and analyzed several times over the course of each sample set. Retention times of all sample peaks falling in the range of the PNA marker compounds [$RRI_{\text{biphenyl}} = 100$, $RRI_{\text{phenanthrene}} = 200$, $RRI_{\text{pyrene}} = 300$, $RRI_{\text{chrysene}} = 400$, $RRI_{\text{perylene}} = 500$, $RRI_{\text{benzo(ghi)perylene}} = 600$] were automatically calculated using the HP 3356 Laboratory Automation System. When long series of runs were scheduled, as was the case with the 56 effluent extracts, PNA marker standards were analyzed at frequent intervals to monitor any retention time shifts. When slight fluctuations did occur, the relative retention time data were corrected for these shifts.

The method adopted by MRC uses the RRIs based on a group of PNA marker compounds used by the VIMS group. This approach is very similar to the Kovats indices developed in 1965 by E. Kovats [8]. A similar approach is also discussed by L. S. Ettre [9-11].

[8] E. Kovats, *Advances in Chromatography*, Vol. 1, J. C. Gidding and R. A. Keller, eds. Marcel Dekker, Inc., New York, New York, 1965. pp. 229.

[9] L. S. Ettre, *Chromatographia*, 6:489, 1973.

[10] L. S. Ettre, *Chromatographia*, 7:39, 1974.

[11] L. S. Ettre, *Chromatographia*, 7:261, 1974.

The strength of the present approach lies in the large amount of data presently available at VIMS on Chesapeake Bay sediment and fish tissue extract analyses. The data presented in the present section show the strength of this approach when using state-of-the-art GC/FID and GC/MS instrumentation. However, other capillary chromatographic/specific detector instrumentation (i.e., GC/EC, GC/Hall, GC/PID, etc.) may also be used for screening large amounts of sample extracts, and these data can also be easily correlated with capillary GC/MS data through the use of RRIs generated using the MRC protocol. The major weakness, however, of this approach is the choice of the PNA marker compounds. A much more versatile index such as the Kovats Retention Index (KRI), or that developed by M. Lee [12], eliminates the problem of components eluting before biphenyl or after benzo(ghi)perylene. In the present study, if our approach had been the use of Kovats Retention Indices, all data obtained could be assigned KRIs, since the latter index is limited only by the high molecular weight limit of the chromatographic analysis system. However, components eluting in the first half of the TCO region could not be assigned RRIs, since they eluted before the elution time of biphenyl. The following sections show how the RRIs generated within the present study could be used for the screening of sample extracts of interest to the Chesapeake Bay Program, and address several problems in the implementation of this approach.

C.10.1 RRIs of Deuterated Spiking Compounds

In order to evaluate how reproducible the present RRI approach is in the analysis of real sample extracts, RRIs of the deuterated surrogate spiking compounds present in each extract were compared for all effluent and sediment extracts. Tables C.10-1 through C.10-4 show the RRIs calculated for pyrene-d₁₀, chrysene-d₁₂, and

[12] Lee, M. L., D. L. Vossilaros, C. M. White, and M. Novotny, Anal. Chem., 51:768, 1979.

TABLE C.10-1. RELATIVE RETENTION INDICES FOR THREE SURROGATE SPIKING COMPOUNDS IN PHASE III EFFLUENTS

Spike compound	MRC Effluent workup number																
	8182	8183	8184	8185	8186	8188	8191	8192	8193	8194	8204	8205	8206	8207	8208	8209	8210
Pyrene-d ₁₀	299.12	299.28	299.46	1 ^a	300.04	298.22	298.36	298.21	297.42	297.99	298.24	298.01	298.11	298.66	297.84	298.18	298.42
Chrysene-d ₁₂	398.02	397.71	397.98	398.24	398.50	397.23	397.37	397.42	396.69	397.11	397.37	397.22	397.30	397.42	396.83	397.44	397.53
Perylene-d ₁₂	497.54	497.94	498.40	NP ^b	499.13	497.40	497.36	497.48	NP	NP	497.14	497.22	497.36	497.26	496.44	497.44	497.14

	MRC Effluent workup number												Average	Range ^c	Standard deviation	
	8211	8212	8217	8218	8219	8225	8230	8233	8237	8238	8239	8240				8245
Pyrene-d ₁₀	298.41	298.98	298.23	298.36	298.33	298.34	298.25	298.51	298.25	298.09	298.72	298.64	298.46	298.43	±1.61	0.53
Chrysene-d ₁₂	397.41	398.29	396.86	397.13	397.07	397.16	397.19	397.28	397.42	397.07	397.50	397.31	397.39	397.39	±1.11	0.41
Perylene-d ₁₂	497.24	497.98	496.90	497.21	497.01	496.99	497.23	497.27	497.04	497.05	497.26	497.22	497.43	497.34	±1.79	0.51

^aInterference present.^bNo peak, or peak below detection limit.^cRange = ±[(Value showing greatest deviation from average) - (average)].

TABLE C.10-2. RELATIVE RETENTION INDICES FOR THREE SURROGATE SPIKING COMPOUNDS IN PHASE III EFFLUENT SPIKING STANDARD

Spike compound	MRC Raw file no. for each analysis					Average	Range ^a	Standard deviation
	BAY6	BAY30	BAY58	BAY80	BAY105			
Pyrene-d ₁₀	298.54	297.96	299.96	298.56	298.80	298.76	±1.20	0.74
Chrysene-d ₁₂	397.41	396.75	398.97	397.40	397.66	397.64	±1.33	0.82
Perylene-d ₁₂	497.48	496.52	498.67	497.06	497.70	497.47	±1.20	0.80

^aRange = ±[(Value showing greatest deviation from average) - (average)].

TABLE C.10-3. RELATIVE RETENTION INDICES FOR THREE SURROGATE SPIKING COMPOUNDS IN PHASE III SEDIMENTS

Spike compound	MRC Sediment workup number												
	8377	8379	8380	8381	8382	8383	8384	8385	8386	8387	8393	8394	8395
Pyrene-d ₁₀	298.62	299.40	I ^a	299.65	299.09	298.82	298.99	298.67	298.74	298.86	298.45	298.58	298.45
Chrysene-d ₁₂	397.68	398.64	I	399.34	398.38	397.98	398.46	397.71	397.91	397.83	397.50	397.55	397.27
Perylene-d ₁₂	498.07	498.94	I	498.99	498.73	497.97	498.79	498.12	498.29	498.17	497.84	497.63	497.35

	MRC Sediment workup number									Average	Range ^b	Standard deviation
	8396	8400	8401	8402	8403	8404	8405	8406	8407			
Pyrene-d ₁₀	298.83	298.67	298.70	298.68	298.62	298.66	298.66	298.67	298.70	298.79	±0.86	0.29
Chrysene-d ₁₂	398.25	397.75	397.69	397.75	397.68	397.76	397.77	397.79	397.84	397.93	±1.41	0.46
Perylene-d ₁₂	497.98	497.85	497.88	497.77	497.79	497.76	497.86	497.78	497.83	498.07	±0.92	0.44

^aInterference present.

^bRange = ±[(Value showing greatest deviation from average) - (average)].

TABLE C.10-4. RELATIVE RETENTION INDICES FOR THREE SURROGATE SPIKING COMPOUNDS IN PHASE III SEDIMENT SPIKING STANDARD

Spike compound	MRC Raw file no. for each analysis						Average	Range ^a	Standard deviation
	CBS6	CBS16	CBS32	CBS35	CBS46	CBS23			
Pyrene-d ₁₀	298.25	298.90	298.64	298.50	298.52	298.51	298.55	±0.35	0.21
Chrysene-d ₁₂	397.07	397.69	397.54	397.56	397.66	397.44	397.49	±0.42	0.23
Perylene-d ₁₂	497.05	498.10	497.68	497.68	497.75	497.50	497.63	±0.58	0.34

^aRange = ±[(Value showing greatest deviation from average) - (average)].

perylene-d₁₂ in 30 effluent sample extracts, 5 effluent spiking standards, 22 sediment extracts, and 6 sediment spiking standards analyzed by the GC/FID method. The standard deviations of all of these values range from 0.21 to 0.82 RRI units and appear to be independent of sample matrix effects. For example, the average RRIs calculated for the three deuterated compounds are independent of whether the matrix is a clean spiking standard or a highly contaminated extract of an effluent or sediment sample.

Similar data are shown for RRIs of pyrene-d₁₀, chrysene-d₁₂, perylene-d₁₂, and anthracene-d₁₀ calculated from GC/MS analyses of effluent and sediment extracts shown in Tables C.10-5 and C.10-6. In fact, the absolute values of the RRIs calculated for a given deuterated surrogate spiking compound are within one unit, whether measured from GC/FID or GC/MS data. It should be emphasized that the RRIs were calculated using external PNA marker compound standards, and not by spiking the matrix with the marker compounds as is the standard protocol followed by the VIMS group. This further shows that the routine analysis of extracts using the instrumentation described within the present report, is highly reproducible (at least for PNAs) and thus allows very accurate determinations of RRIs without contaminating sample extracts with native compounds.

C.10.2 RRIs of Native PNAs

A number of sample extracts were identified, from GC/MS data to contain fluoranthene, phenanthrene, and pyrene. Table C.10-7 summarizes the RRIs calculated for these compounds from GC/MS data (the GC/FID chromatograms were too complex to identify these compounds unambiguously). As can be seen, excellent agreement is observed for the RRIs for fluoranthene and phenanthrene.

TABLE C.10-5. GC/MS RELATIVE RETENTION INDICES FOR FOUR SURROGATE SPIKING COMPOUNDS IN PHASE III EFFLUENTS

Spike compound	Plant number								
	C150D	C169D	B133S	B142S	B141S	B119D	C157D	C164D	B112D
Pyrene-d ₁₀	298.36	298.36	298.36	298.36	297.89	298.36	298.36	298.36	298.83
Chrysene-d ₁₂	397.91	397.91	397.91	397.39	398.70	397.91	397.91	397.91	398.17
Perylene-d ₁₂	498.02	497.52	498.02	498.02	497.52	498.02	498.02	497.27	498.51
Anthracene-d ₁₀	202.34	201.87	201.87	201.87	201.87	201.87	201.87	202.34	202.81

	Plant number					Average	Range ^a	Standard deviation
	C155D	A109	C156D	C161D	B149S			
Pyrene-d ₁₀	298.83	298.36	298.83	299.06	298.59	298.53	±0.64	0.40
Chrysene-d ₁₂	398.17	397.71	398.17	398.17	397.66	397.99	±0.71	0.30
Perylene-d ₁₂	498.51	499.26	498.51	498.51	498.75	498.01	±1.26	0.71
Anthracene-d ₁₀	202.34	202.34	202.34	202.34	201.88	202.14	±0.67	0.30

^aRange = ±[(Value showing greatest deviation from the average) - (average)].

TABLE C.10-6. GC/MS RELATIVE RETENTION INDICES FOR FOUR SURROGATE SPIKING COMPOUNDS IN PHASE III SEDIMENTS

Spike compound	Plant number												
	C161D	C156D	C159D	B112D	C154D	C153D	A109	B113D	B124D	C157D	B119D	C160D	A101
Pyrene-d ₁₀	299.77	299.77	298.83	299.76	299.30	299.30	298.82	298.82	298.82	298.82	298.82	298.82	298.82
Chrysene-d ₁₂	399.22	399.22	398.44	397.14	397.92	398.70	397.66	397.66	397.66	397.66	397.66	397.66	397.66
Perylene-d ₁₂	499.50	499.50	498.76	497.51	498.76	499.50	498.50	498.50	498.50	498.50	498.50	498.50	498.00
Anthracene-d ₁₀	201.88	202.35	202.35	202.35	202.35	201.88	201.88	202.35	201.88	201.88	201.88	201.88	201.88

	Plant number										Average	Range ^a	Standard deviation
	C164D	B126S	B141S	B142S	B143S	C150D	C158D	C151D	C169S				
Pyrene-d ₁₀	299.06	298.35	298.82	298.82	298.35	298.82	298.82	298.82	298.58	298.95	±0.82	0.40	
Chrysene-d ₁₂	397.66	397.40	397.66	398.18	396.88	397.66	397.40	397.66	397.66	397.84	±1.38	0.59	
Perylene-d ₁₂	498.00	498.50	498.75	498.75	497.51	498.50	498.00	498.00	498.24	498.49	±1.01	0.55	
Anthracene-d ₁₀	201.88	201.88	201.88	201.88	202.35	201.88	201.41	201.41	202.84	202.00	±0.84	0.33	

^aRange = ±[(Value showing greatest deviation from the average) - (average)].

TABLE C.10-7. RELATIVE RETENTION INDICES FROM GC/MS DATA
FOR SOME PEAKS IDENTIFIED AS PNAs

Compound identified by GC/MS	Plant no.	Sediment workup no.	GC/MS peak no.	Relative retention index
Fluoranthene	A109	8400	21	284.24
	B112D	8380	10	284.74
	C153D	8382	14	284.74
	C154D	8381	13	284.74
	C159D	8383	11	284.74
	B126S	8384	10	284.25
			Average	284.58
			Range ^a	±0.34
			Standard dev. ^b	0.26
Phenanthrene	B112D	8380	4	199.35
	C153D	8382	9	199.68
	C154D	8381	8	199.68
	C159D	8383	6	199.68
	B126S	8384	7	199.35
			Average	199.55
			Range	0.20
			Standard dev.	0.18
Pyrene	B112D	8380	11	298.59

^aRange = ±[(value showing greatest deviation from average) - (average)].

^bStandard deviation.

C.10.3 RRIs Measured in Two Sediment Extracts

Two extracts from plants B143S and B141S contained large amounts of aromatic compounds substituted with various lengths of long chain hydrocarbons. Figure C.10-1 shows a comparison of the GC/FID and GC/MS chromatograms obtained from analysis of the sediment from plant B143S. Above each major peak are the RRIs calculated from the GC/FID or GC/MS data shown. Values of RRIs calculated from the GC/FID and GC/MS data from plant B141S are shown in parentheses. The good agreement between RRIs generated from GC/MS data and the fair agreement for RRIs from GC/FID data can be seen in this figure. This example comparison of sediment extract data shows at least one problem encountered with the MRC protocol for effluent analyses and also demonstrates the complexity of the general problem of assimilating such large volumes of information into an understandable format which can be used by environmental scientists to study contamination of the Chesapeake Bay Basin.

The major problem encountered with the data shown in Figure C.10-1 is that the RRIs generated from GC/FID data deviate from RRIs generated from GC/MS data by approximately 7 units in the worst case shown in the figure. This is a much larger deviation than was observed for the deuterated surrogate spiking compounds and the native PNAs shown in Tables C.10-1 through C.10-7. The source of this deviation is probably due to column overloading of the sample analyzed by GC/FID which does not occur in the GC/MS analysis. The reason for this difference is that the GC/FID data were generated from the injection of nondiluted extracts while the GC/MS data were generated after first diluting the extracts by a factor of 10. This can be seen from the increased tailing at the onset of the major peaks in the GC/FID chromatogram. However, this is not due to the classical sample overloading phenomenon, since the RRIs calculated from GC/FID data are earlier than those calculated from GC/MS data. Normal peak overloading causes retention time to

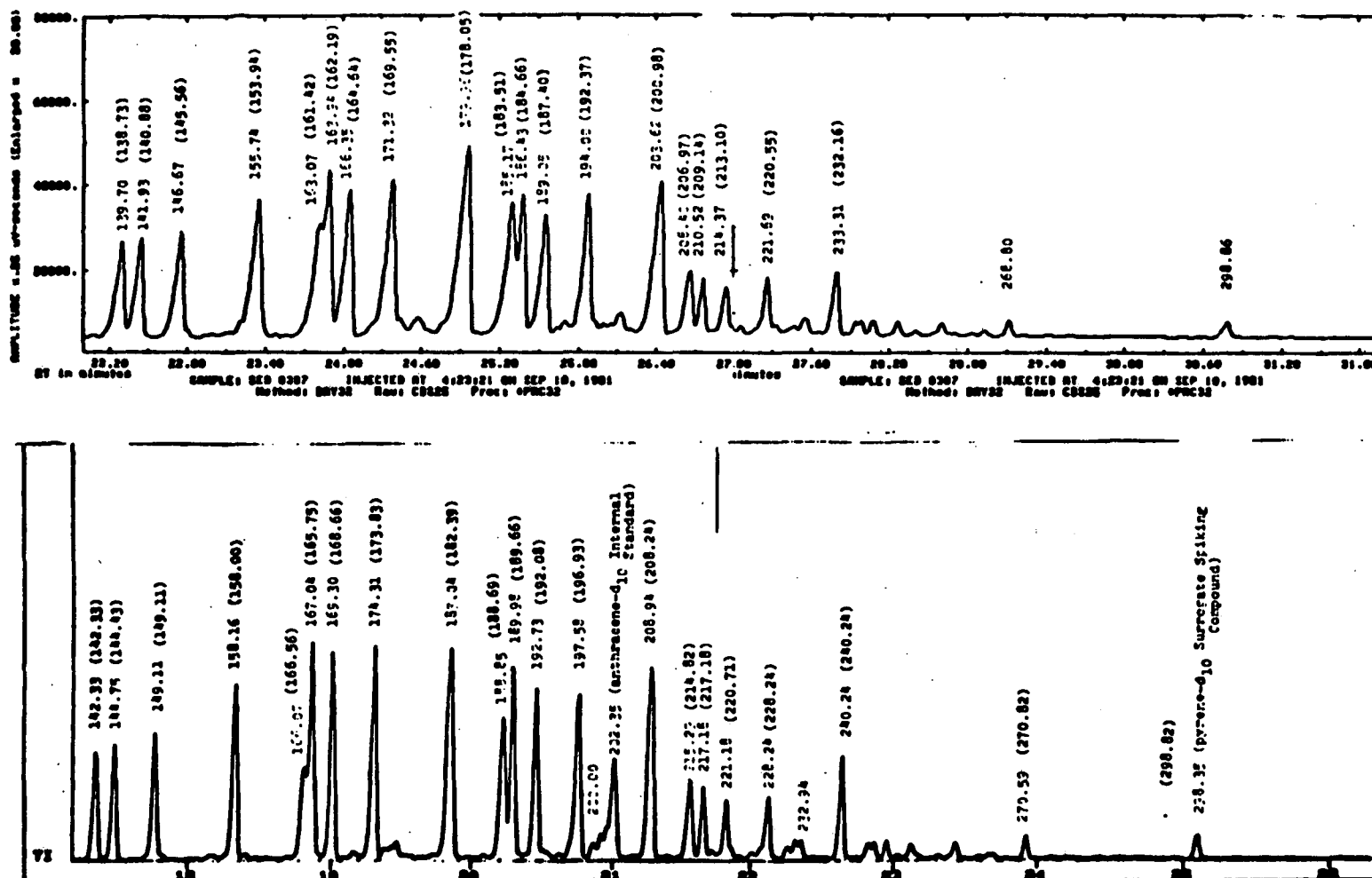


Figure C.10-1. Comparison of capillary chromatograms and relative retention indices obtained from GC/FID and GC/MS analyses of a sediment extract taken from the outfall of a Publicly Owned Treatment Works (POTW).

be shifted to longer retention times [13]. The phenomenon shown in Figure C.10-1 is due to large amounts of organic material being deposited on the chromatographic column which changes the retention characteristics from that of an SE-54 liquid phase to that of the phase containing the organic matrix of the sample. This change is not apparent when examining the RRI's of the nonpolar deuterated PNAs, within the sample, but is apparent when analyzing components which have a large amount of hydrocarbon properties (such as long chain alkyl benzenes) shown in Figure C.10-1. This example shows the necessity to reduce the amount of column overloading by using wide bore capillary columns and also taking care to dilute samples which are known to contain large amounts of chromatographable components.

This example comparison of the GC/FID and GC/MS RRI's for these two plant sediment samples also shows the complexity of the data that are generated from capillary GC/FID and GC/MS analysis of extracts. Even with the highly computerized data acquisition and analysis of samples presently employed in the current study, no effort has been made to easily treat the data once it is acquired and analyzed.

In fact, the time required to display the data shown in Figure C.10-1, transfer RRI's to the figure, and evaluate the data required from 8 to 16 hours of an experienced scientist's time. These data only include 9 minutes of a total of 30 minutes of data collected for the two sediment samples compared. In order to evaluate the results of this total sediment extract analysis in a similar manner would require from 3 to 6 days, or about 1 week (if there were data in this total analysis time). Considering there are approximately 50 effluent extracts (base/neutral and acid) and 22 sediment extracts, a similar comparison of the one sediment extract shown

[13] Fales, H. M. J. Chrom. Sci., 19:26, 1981.

in Figure C.10-1 with these approximately 70 analyses would require more than one-year's time of an experienced scientist. However, to compare all extracts with the 70 analyses would require approximately 70 years to evaluate in a similar manner.

The above calculation is obviously of a worst case and certain assumptions can be made to reduce the numbers of comparisons required. However, it does demonstrate why any detailed analysis of the capillary data generated is virtually impossible unless selected analytes are chosen (such as the PNAs as chosen by the VIMS group), or unless sophisticated pattern recognition approaches are employed which reduce the time required for a given comparison.

An interim solution to data interpretation is presently being employed by VIMS (Hugett, et al.) where they search effluent and sediment RRI data for components which they have compiled in a file of known RRIs. However, it should be recognized that this approach still limits the comparisons to those components which are within the file of known RRIs. This obviously reduces the data analysis time, but at the cost of limiting the analysis to a finite number of components.

A more complete analysis approach for data interpretation by the Chesapeake Bay Office would be to develop pattern recognition approaches for the treatment of chromatographic data, similar to that developed by Sweeley [14] and Bieman [15] for biological profiling of body fluids. The general subject of pattern recognition approaches to a wide variety of chromatographic analyses is not new and is also the subject of a recent symposium given by the Ohio Valley Chromatography Symposium (June 1982). Not until these

[14] Sweeley, C. C., N. D. Young, J. F. Holland, and S. C. Gates, J. Chrom., 99:507, 1974.

[15] Nau, H., and K. Bieman. Anal. Chem., 46:426, 1974.

methods can be used for data screening (which can also be applied to all types of analytical and toxicological data) of very complex environmental samples, will real progress be made in understanding the sources and potential threats of a wide variety of industrial discharges to the Chesapeake Bay Basin.

C.11 GC/MS ANALYSES OF EXTRACTABLE ORGANICS

C.11.1 Introduction

All GC/MS analyses were performed by automated capillary column chromatography using a Hewlett-Packard 5985-A GC/MS with a 5934 data system, which used Revision C Software and included a 7920 multi-drive disc unit. Since the peaks obtained in capillary column GC/MS analysis are only a few seconds wide (much narrower than packed-column peaks), it is necessary to scan the mass spectrometer at its maximum rate to generate reliable mass spectra -- approximately 4500 spectra for a 40-minute run, depending on the initial MS scan delay, as compared to perhaps 700 for a 40-minute, packed-column run. A low detection threshold must also be used to capture the information contained in small peaks, which combines with the large number of spectra to consume enormous amounts of computer disc space in a given analysis. In some cases several GC/MS analyses could fill a data disc cartridge. Thus, to perform a series of 10 to 20 analyses, using the automatic injector system, requires the use of several discs for data acquisition. This is only possible in an automated mode on the Hewlett-Packard system by using the multi-disc drive in which the equivalent of up to 19 discs could be accessed simultaneously.

C.11.2 Method

The relevant GC/MS parameters used for the Phase III analyses are summarized below:

- 30 m fused silica SE-54 WCOT column
- Column head pressure, 7-9 psi
- MS operating pressure, 1×10^{-5} to 4×10^{-6} torr
- Septem purge on at 0.5 min
- Initial temperature, 50°C
- Initial temperature held for 4 minutes
- Heating rate, 8°C/min
- Final temperature, 280°C

- Total analysis time, 40 min
- Injector, splitless mode, temperature, 250°C
- Transfer line temperature, 250°C (fused silica column through this zone, directly to the MS source)
- Electron energy, 70eV
- Source temperature, 200°C
- A/D rate, 1 measurement/0.125 amu;
scan rate, approximately 0.6 s/scan
- Mass spectrometer scan delay, 3.0 min

The routine procedure used for GC/MS analysis was to transfer 150 µL of the sample extract into 1.5 mL sample vials along with 150 µL of a 100 µg/mL anthracene-d₁₀ in methylene chloride internal standard. The vial was capped and placed in the autosampler, which injected approximately 1 µL into the GC, operating in the splitless mode.

C.11.3 Interpretation of Mass Spectra

The following protocol was followed in interpreting the mass spectral data obtained from the Phase III extracts:

- 1) Spectra of compounds detected as peaks in the Hewlett-Packard BATCH program with a 1% to 5% threshold (depending upon the complexity of the sample) were automatically compared with standard spectra in the computerized EPA/NIH mass spectral data base using the Probability Based Search (PBS) software supplied by Hewlett-Packard. A goodness of fit parameter was generated (1.0 being a perfect match) for the ten matches closest to 1.0.
- 2) The results from these searches were reviewed by an experienced mass spectroscopist using the Hewlett-Packard supplied spectral comparison software, SPDIF, to compare the sample spectra with the standard spectra identified by the SEARCH program.

- 3) In cases where the spectral agreement was judged to be adequate, compound identities were assigned. When compound isomers produced similar spectra, no specific isomer could be identified based solely upon mass spectral data.
- 4) In cases where the agreement was not adequate, identifications were made on the basis of manual interpretation (when obvious), or compounds were listed as unknown with their major masses given in parentheses. If a high even mass was present with odd fragment masses, the even mass was underlined to indicate a possible molecular ion.

The approach outlined above was adopted to minimize the cost and time required for the analyses of large amounts of capillary chromatographic mass spectra by maximizing the use of computerized data interpretation techniques.

To illustrate the use of this protocol, a section of a total ion chromatogram is reproduced in Figure C.11-1. The mass spectrum from the chromatographic peak designated by the arrow was automatically compared with the spectra in the EPA/NIH mass spectral data base using available Hewlett-Packard software options. The output from this search is illustrated in Table C.11-1. The location of the unknown spectrum which was searched is shown in the table as spectrum number 12 in File Reference Number (FRN) 23121. This latter data file was generated from the Hewlett-Packard BATCH Quantification program which measured the areas of peaks present in the total ion chromatogram of the original capillary GC/MS data located in FRN 13121.

Library 3000 listed in Table C.11-1 refers to the EPA/NIH Mass Spectral Data Base (NSRDS-NBS 63) mass spectral library of over 30,000 compounds. The PBS SEARCH output shown in the table indicates that 28,767 spectra were searched and seven probable identifications were found. The seven "hits" are listed in

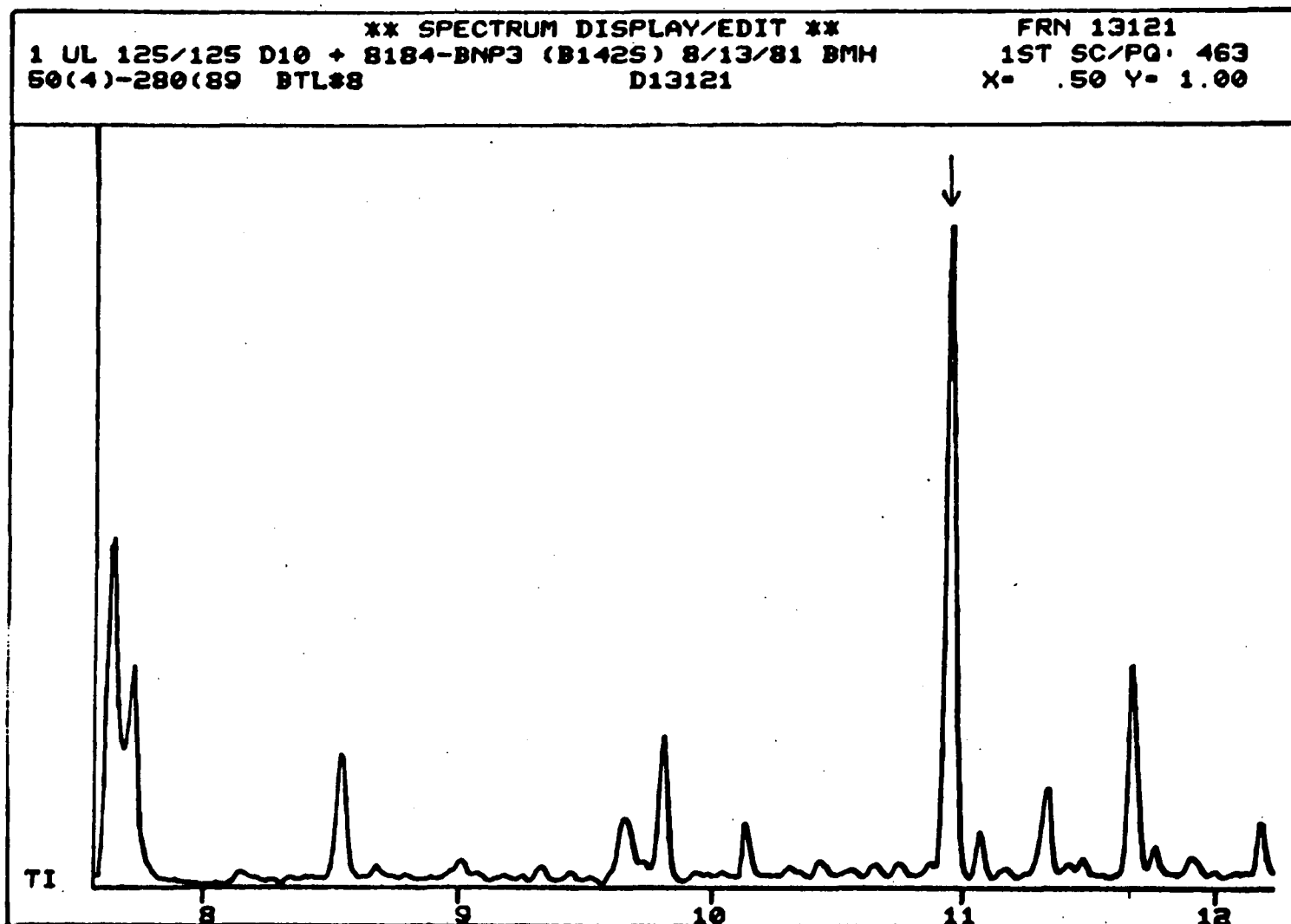


Figure C.11-1. Portion of total ion chromatogram obtained from the analysis of the base/neutral fraction from the effluent of Plant B142S.

TABLE C.11-1. EXAMPLE OF THE OUTPUT OF THE HEWLETT-PACKARD
PBS SEARCH PROGRAM USED TO IDENTIFY COMPONENTS
IN EFFLUENT AND SEDIMENT EXTRACTS

REF. SPECT # = 12 LSN = 12. MW = 0 FRN = 23121 RET. TIME = 11.0
92 PEAKS, 24 SIGNIFICANT MAX K 23.8

LIBRARY 3000 28767 SPECTRA SEARCHED, 7 HIT(S)

.9779 + Benzene, 1,2,3-trichloro- (8CI9CI)
SPEC = 4698 LSN = 10457. MW = 180 C6H3Cl3
FRN = 3005 [NBS 10458.] CAS # 0000087616 EPA # 0000027788
MATCHING PEAKS CONTAMINATED MISSING PEAKS QUAL INDEX = 629
20.0 9 54% .0 0 0% .0 0 0% MULTIPLIER = .74

.9778 + Benzene, 1,2,4-trichloro- (8CI9CI)
SPEC = 4700 LSN = 10459. MW = 180 C6H3Cl3
FRN = 3005 [NBS 10460.] CAS # 0000120821 EPA # 0000027871
MATCHING PEAKS CONTAMINATED MISSING PEAKS QUAL INDEX = 728
20.0 9 51% .0 0 0% .0 0 0% MULTIPLIER = .92

.9777 + Benzene, 1,3,5-trichloro- (8CI9CI)
SPEC = 4699 LSN = 10458. MW = 180 C6H3Cl3
FRN = 3005 [NBS 10459.] CAS # 0000108703 EPA # 0000022208
MATCHING PEAKS CONTAMINATED MISSING PEAKS QUAL INDEX = 692
19.8 9 50% .0 0 0% .0 0 0% MULTIPLIER = .83

.9041 * Benzene, 1-bromo-3,5-dichloro- (3CI9CI)
SPEC = 4882 LSN = 15755. MW = 224 C6H3BrCl2
FRN = 3008 [NBS 15757.] CAS # 0019752557 EPA # 0000010686
MATCHING PEAKS CONTAMINATED MISSING PEAKS QUAL INDEX = 699
15.2 7 25% .0 0 0% 3.1 1 16% MULTIPLIER = .57

.6274 * Benzene, 2-bromo-1,4-dichloro- (3CI9CI)
SPEC = 4880 LSN = 15753. MW = 224 C6H3BrCl2
FRN = 3008 [NBS 15755.] CAS # 0001435503 EPA # 0000010687
MATCHING PEAKS CONTAMINATED MISSING PEAKS QUAL INDEX = 655
15.2 7 24% .0 0 0% 8.1 3 33% MULTIPLIER = 1.04

.6182 * Benzaldehyde, 3,4-dichloro- (8CI9CI)
SPEC = 3872 LSN = 9631. MW = 174 C7H4Cl2O
FRN = 3005 [NBS 9632.] CAS # 0006287383 EPA # 0000007043
MATCHING PEAKS CONTAMINATED MISSING PEAKS QUAL INDEX = 649
15.0 7 25% .0 0 0% 8.3 3 34% MULTIPLIER = .71

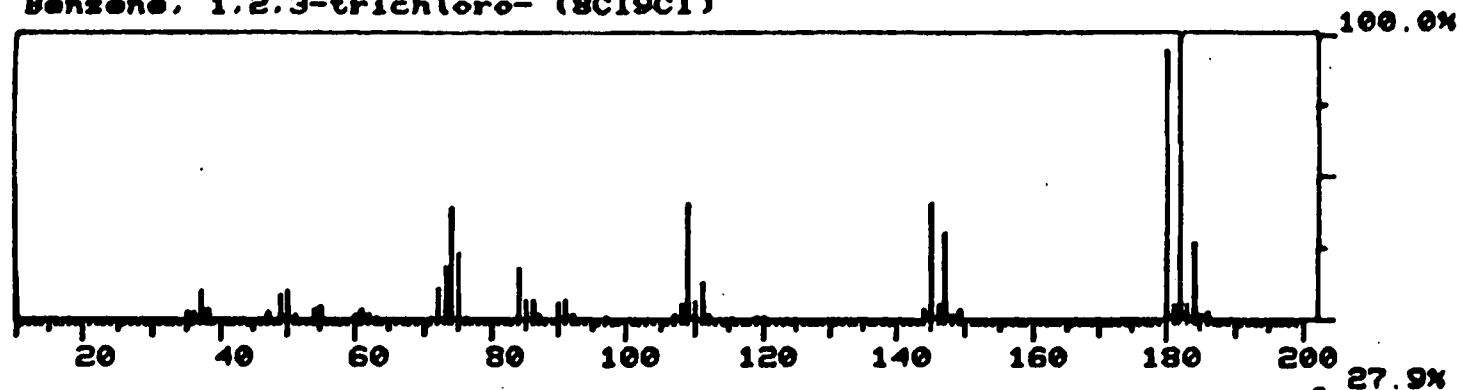
.6138 * Benzaldehyde, 2,4-dichloro- (8CI9CI)
SPEC = 3871 LSN = 9630. MW = 174 C7H4Cl2O
FRN = 3005 [NBS 9631.] CAS # 0000874420 EPA # 0000007042
MATCHING PEAKS CONTAMINATED MISSING PEAKS QUAL INDEX = 655
15.0 7 23% .0 0 0% 8.3 3 45% MULTIPLIER = .95

decreasing match order. For each identified compound, the goodness of fit value (with 1.0 being a perfect match), is followed by the compound name and additional information relating to the location of the standard spectrum and additional parameters calculated as a part of the PBS SEARCH program.

Spectral comparison plots were generated from those "best fit" candidate compounds identified in the computerized search using the Hewlett-Packard SPDIF program. Three examples of comparisons of standard library spectra of three of the four most likely candidate compounds with the actual spectrum obtained in the analysis of the extract are shown in Figures C.11-2, C.11-3, and C.11-4. Figures C.11-2 and C.11-3 show comparisons of two different trichlorobenzene isomers with the unknown spectrum. From the difference of each of the two spectra plotted in these figures, it can be seen that less than 30% deviations with the two standard spectra were measured. Since the two standard spectra of trichlorobenzene isomers are very similar, the identification of the peak at 11.0 minutes is listed in the effluent table for this plant as "Benzene, trichloro-(isomer)." Figure C.11-4 gives an example of the comparison of a compound listed as a possible identification, with the spectrum of the compound eluting at 11.0 minutes. The fact that the difference spectrum shows 100% deviations, indicates that the particular computer identification given is incorrect.

These comparative mass spectral plots were reviewed by an expert mass spectroscopist who, based on experience in mass spectrometry and mass spectral interpretation, accepted or rejected the computer-generated identification. In the example, trichlorobenzene (isomer) was determined to be the proper identification for the compound in question. It should be emphasized that this identification is considered to be tentative until confirmed by the measurement of its relative retention time of an authentic standard of isomers of the identified compound using similar

FRN 3004 SPECTRUM 4698 MU- 180 C6H3Cl3
Benzene, 1,2,3-trichloro- (8CI9CI)



FRN 23121 SPECTRUM 12 RET. TIME: 11.0
1 UL 125/125 D10 + 8184-BNP3 (B1425) 8/13/81 BMH DRN# 13121

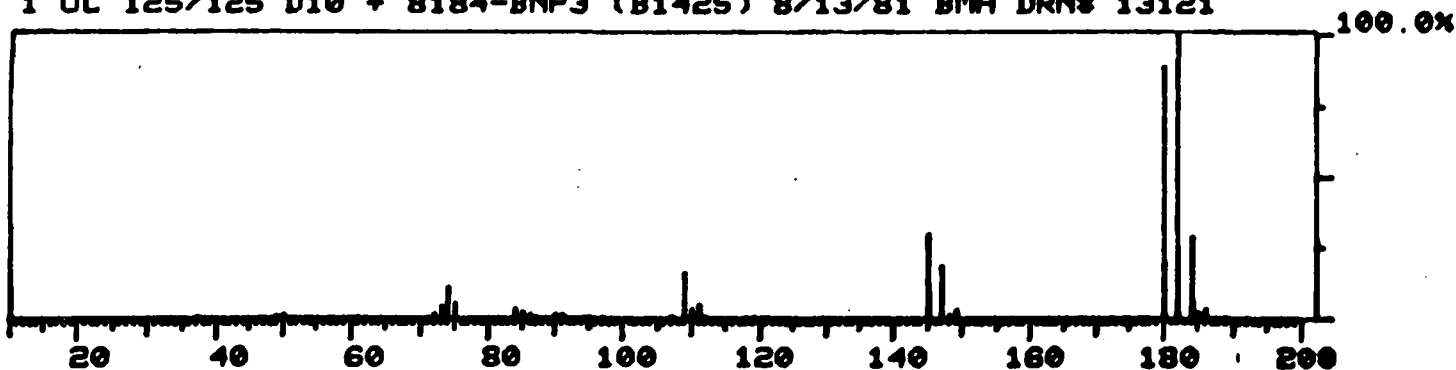
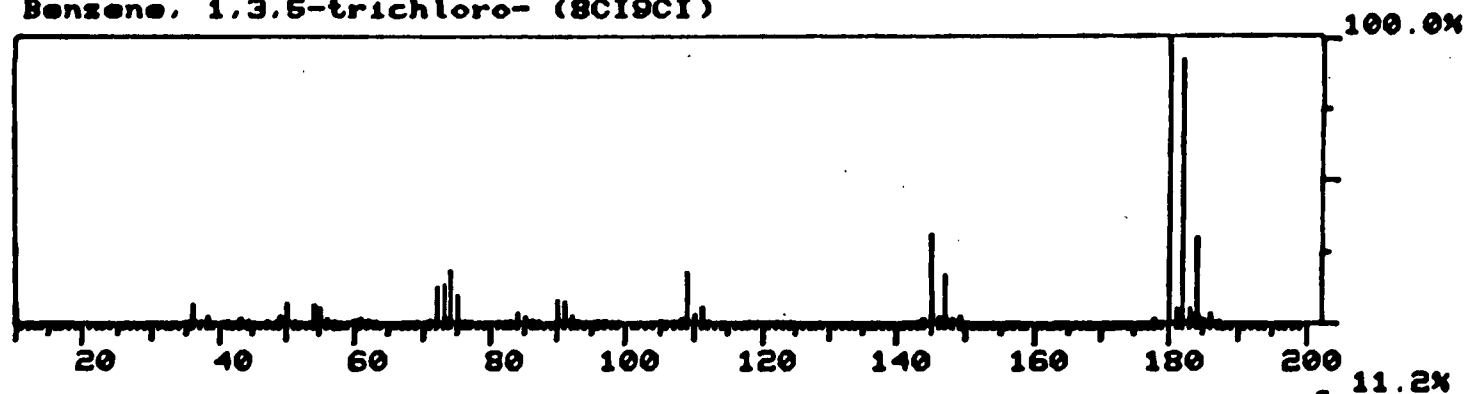


Figure C.11-2. Comparison of the mass spectrum of the highest matching compound shown in Table C.11-1 with that of the unknown compound eluting at 11.0 minutes and shown in Figure C.11-1.

FRN 3004 SPECTRUM 4699 MW- 180 C6H3Cl3
Benzene, 1,3,5-trichloro- (8CI9CI)



FRN 23121 SPECTRUM 12 RET. TIME: 11.0
1 UL 125/125 D10 + 8184-BNP3 (B142S) 8/13/81 BMH DRN# 13121

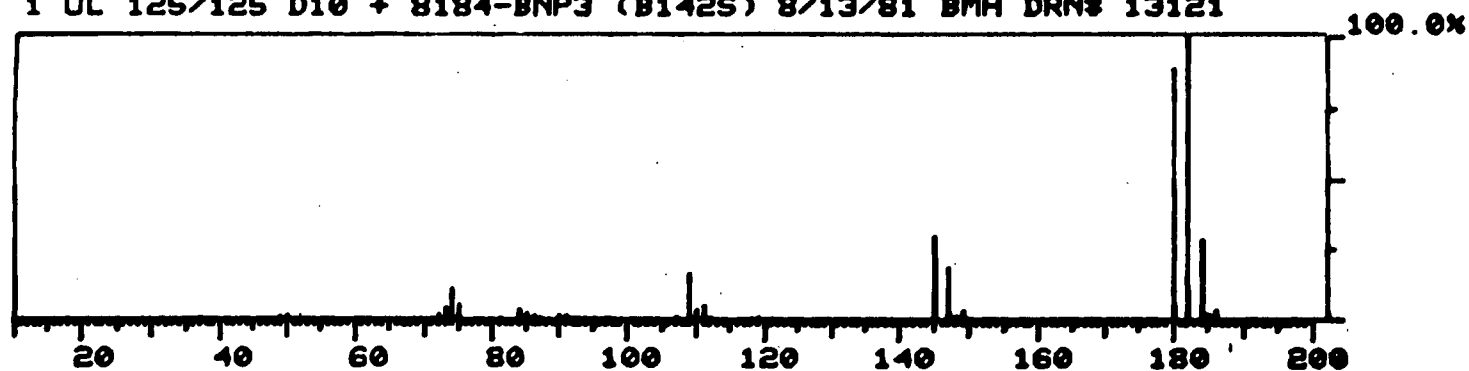
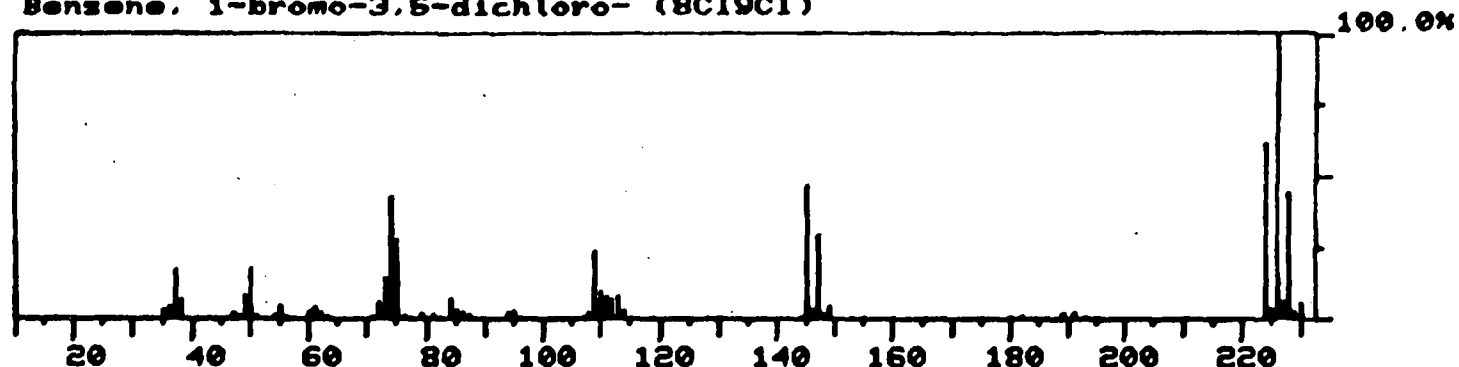


Figure C.11-3. Comparison of the mass spectrum of the third highest matching compound shown in Table C.11-1 with that of the unknown compound eluting at 11.0 minutes and shown in Figure C.11-1.

FRN 3007 SPECTRUM 4882 MU- 224 C6H3BrCl2
Benzene, 1-bromo-3,5-dichloro- (8CI9CI)



FRN 23121 SPECTRUM 12 RET. TIME: 11.0
1 UL 125/125 D10 + 8184-BNP3 (B142S) 8/13/81 BMH DRN# 13121

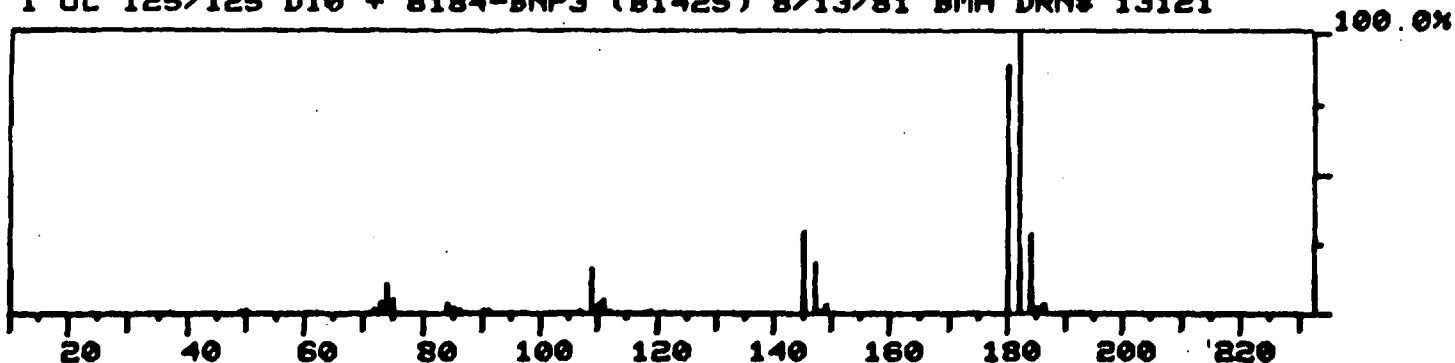


Figure C.11-4. Comparison of the mass spectrum of the fourth highest matching compound shown in Table C.11-1 with that of the unknown compound eluting at 11.0 minutes and shown in Figure C.11-1.

analytical conditions as those used for the original sample extract analysis.

Some considerations that go into making decisions on the identity of components in effluent and sediment extracts include:

- 1) Unknown spectrum contains all peaks with intensities greater than 10% of the base peak in the standard spectrum.
- 2) All mass intensities of multiplets present in the standard spectrum must also be present in the unknown spectrum with similar relative intensities.
- 3) Since the DFTPP spectrum in the low mass region is lower than that given in the EPA criterion for this compound (see Section C.11.5), quantitative agreement of ion intensities was not required for masses below m/e 60. For example, Figure C.11-5 compares the spectrum for pentadecane found in plant B124D sediment extract with that published in the EPA/NIH mass spectral library. As can be seen, while the multiplets at m/e 43, 57, and 71 are present in both spectra, the relative intensities for the lower masses in the spectrum generated during Phase III are approximately 50% of those shown in the standard mass spectral library. However, this does not prevent the correct identification of this compound.
- 4) If peaks are present additional to those in the standard spectrum of a compound, then it is assumed that the additional peaks are due to the presence of an unknown co-eluting compound. In obvious cases of mixed spectra, the PBS SEARCH program identified the presence of a mixture of spectra with a "+" in the column following the match factor. Where mixed spectra are confirmed using the spectral comparison program, the major identified compound was listed along with an estimate of the percent of the unknown compound present in the mixed spectrum.

C.11-11

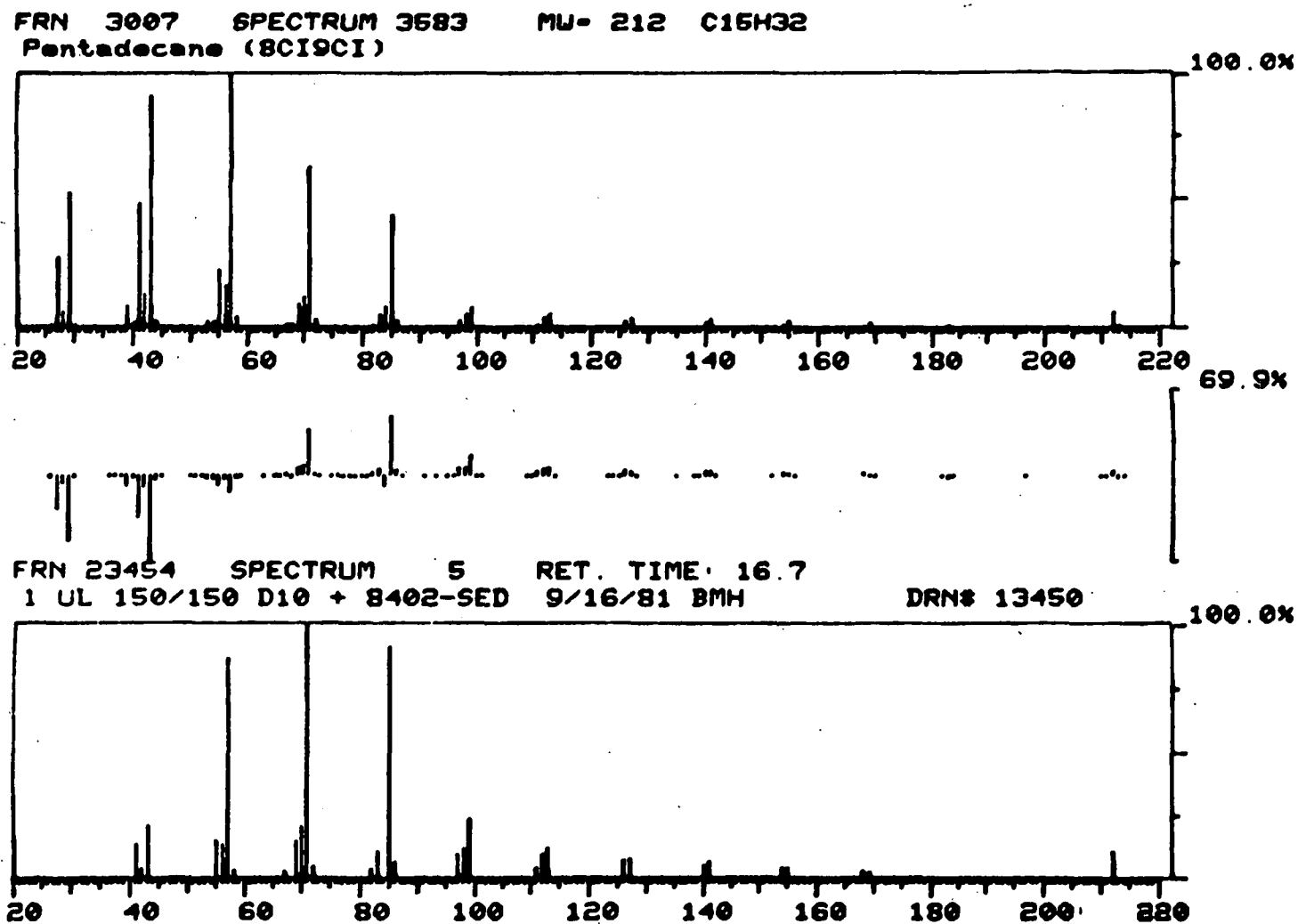


Figure C.11-5. Comparison of the EPA/NIH Library Spectrum of pentadecane with the compound eluting at 16.7 minutes in Plant B124D sediment extract.

Several mass spectra from Phases II and III are shown here to illustrate those obtained. Figures C.11-6 (Acenaphthylene) and C.11-7 (C₁-naphthalene) show the quality of spectra obtained for most of the compounds identified using the PBS SEARCH program. Figures C.11-8 and C.11-9 show the spectra of substances which could not be identified. Due to the large amounts of time generally required to identify unknown compounds which are not in the EPA/NIH mass spectral library, no attempt was made to manually determine the structures of compounds not identified using computer search techniques. However, attempts were made to give additional information such as the major masses found in the unknown, the molecular weight if the spectrum appears to contain a molecular ion, and the presence of nonhydrocarbon atoms. However, the identification of the presence of chlorine, sulfur, or silicon in unknown compounds is based solely upon the occurrence of multiplet ion patterns which are consistent with the naturally-occurring abundances of isotopes for these species, and is used only to give more information about the unknown compound's spectrum.

The good chromatography generally observed in most water effluent analyses resulted in relatively pure mass spectra being obtained for most compounds detected in water. However, many sediment extracts contained a very broadly eluting component or components which resulted in spectra containing ions from the broadly eluting components and the narrowly eluting compounds. An example of this is shown in Figures C.11-10 and C.11-11. The mass spectrum obtained at the retention time marked by the arrow in Figure C.11-10 is shown in C.11-11. As can be seen from the mass spectrum, masses 83, 97, and 109 are major ions in the spectrum. Figure C.11-10 also shows the response of these three masses as a function of chromatographic elution time. This display shows that the major ion chromatograms of the unknown component or components, eluting as a very broad hump, have similar shapes as does the broad hump in the total ion chromatogram. Therefore,

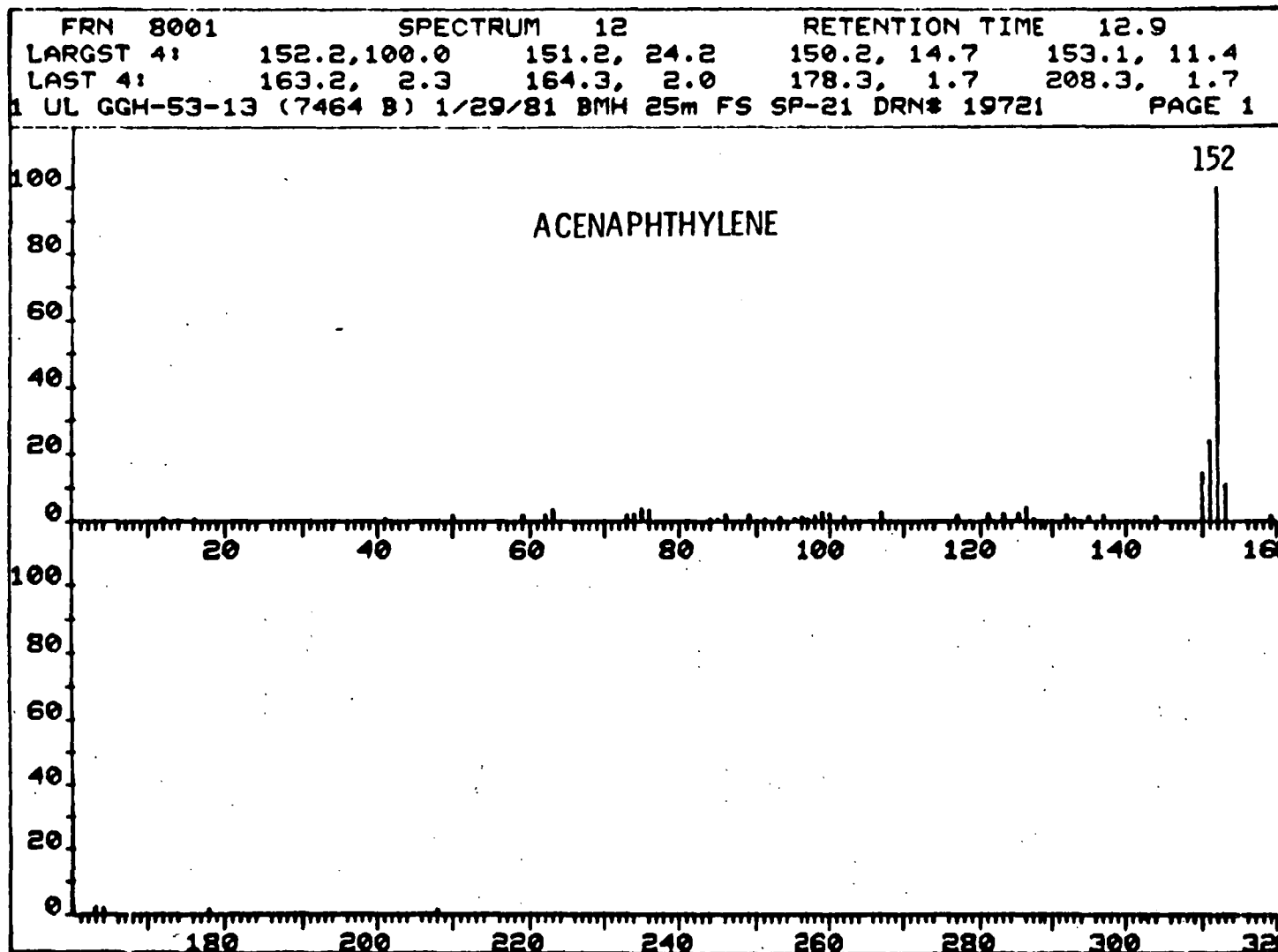


Figure C.11-6. Mass spectrum of acenaphthylene identified by comparison with an authentic standard.

C.11-13

WORK AREA SPECTRUM FRN 19719 PAGE 1 Y = 1.00
 LARGST 4: 142.1, 100.0 141.1, 89.7 115.2, 23.1 143.1, 10.0
 LAST 4: 143.1, 10.0 152.0, 2.3 207.1, 1.4 215.3, 2.5
 + 788 + 789 -784 -783

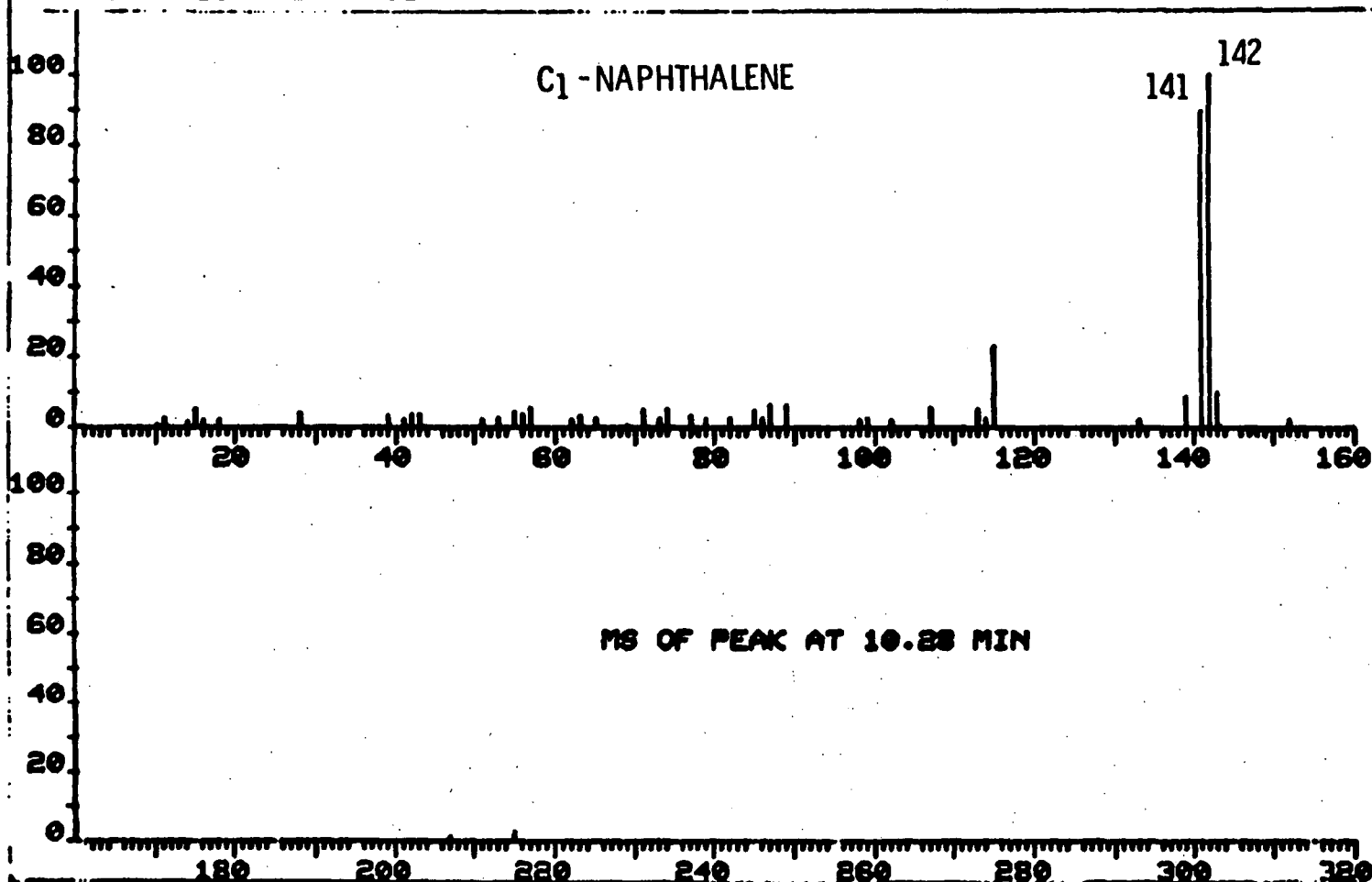


Figure C.11-7. Mass spectrum of C₁-naphthalene, tentatively identified by comparison with a reference spectrum.

C.11-14

FRN 13132	SPECTRUM 629		RETENTION TIME 9.1	
LAPST 4:	86.2, 100.0	72.2, 24.2	101.2, 22.4	57.3, 19.7
LAST 4:	173.2, 1.4	174.3, .1	354.2, .0	446.3, .0
PAGE 1 Y = 1.00				

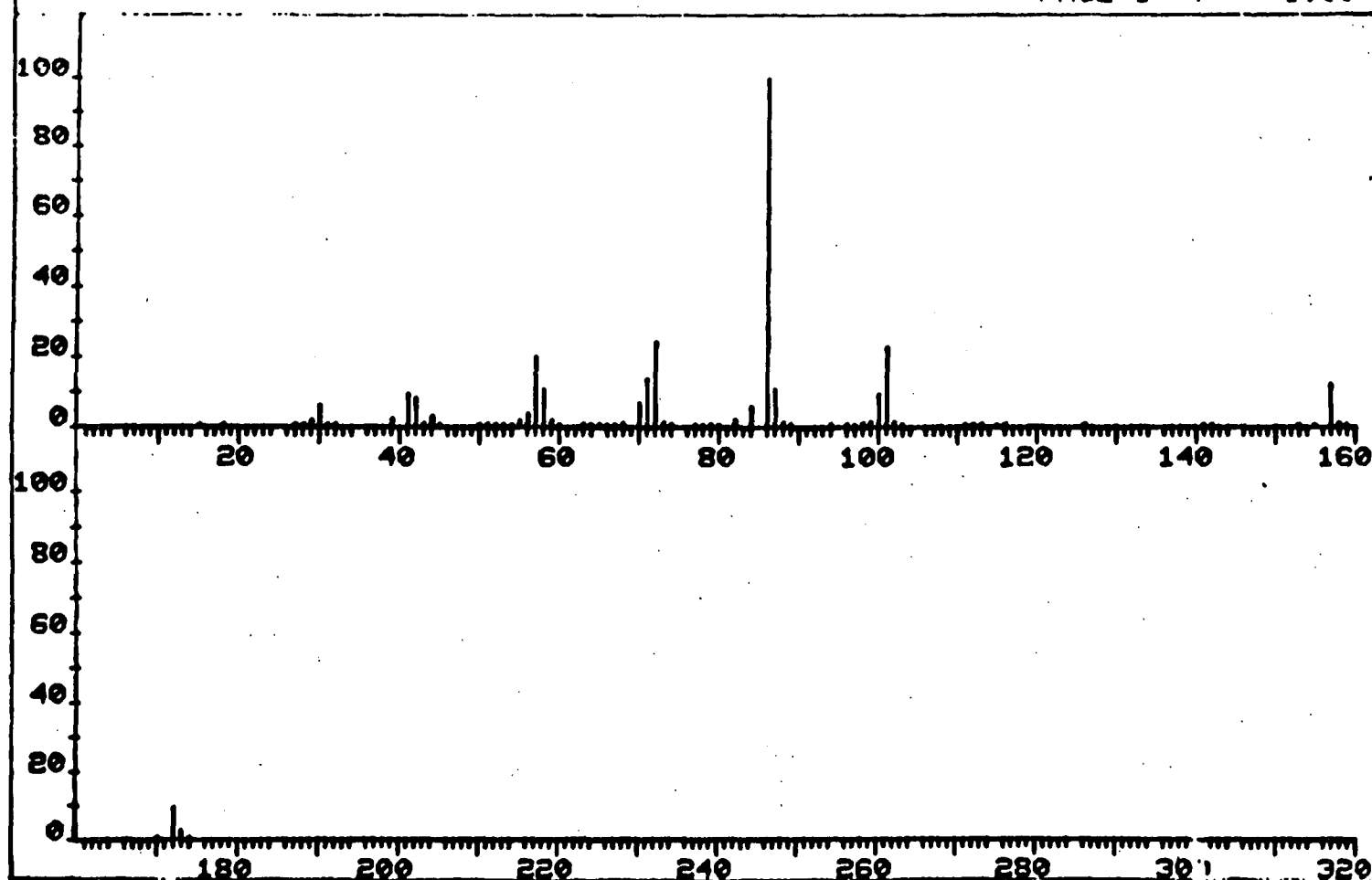


Figure C.11-8. Mass spectrum of unknown compound eluting at 9.1 minutes in plant A109 effluent base/neutral extract.

FRN 13448	SPECTRUM 2285		RETENTION TIME 24.9	
LARGST 4:	216.1, 100.0	71.2, 56.7	85.2, 56.3	57.2, 45.2
LAST 4:	212.0, 31.8	216.1, 100.0	217.0, 23.4	218.1, 14.6
PAGE 1 Y = 1.00				

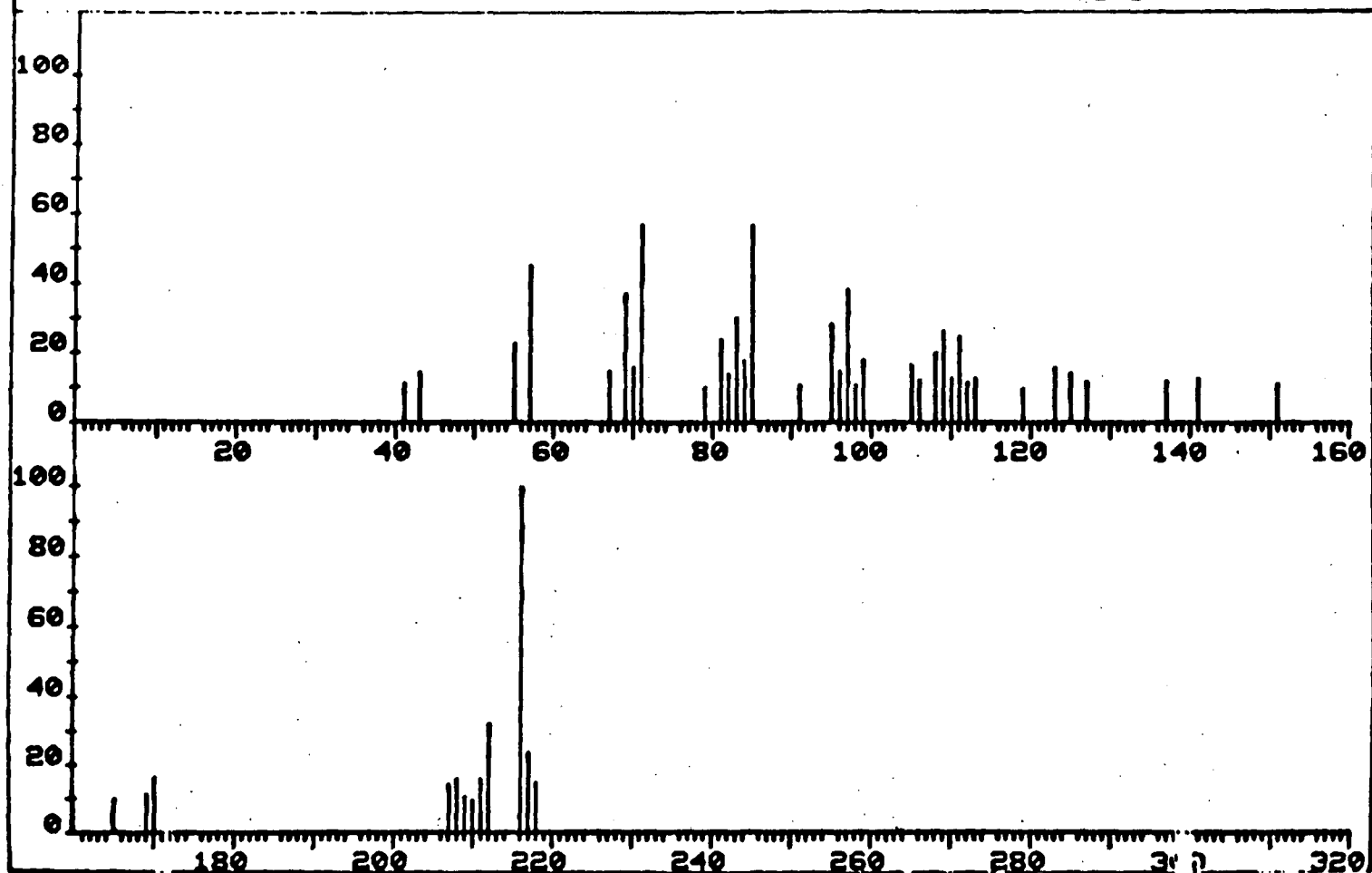


Figure C.11-9. Mass spectrum of unknown compound eluting at 24.9 minutes in Plant A109 sediment extract.

C.11-16

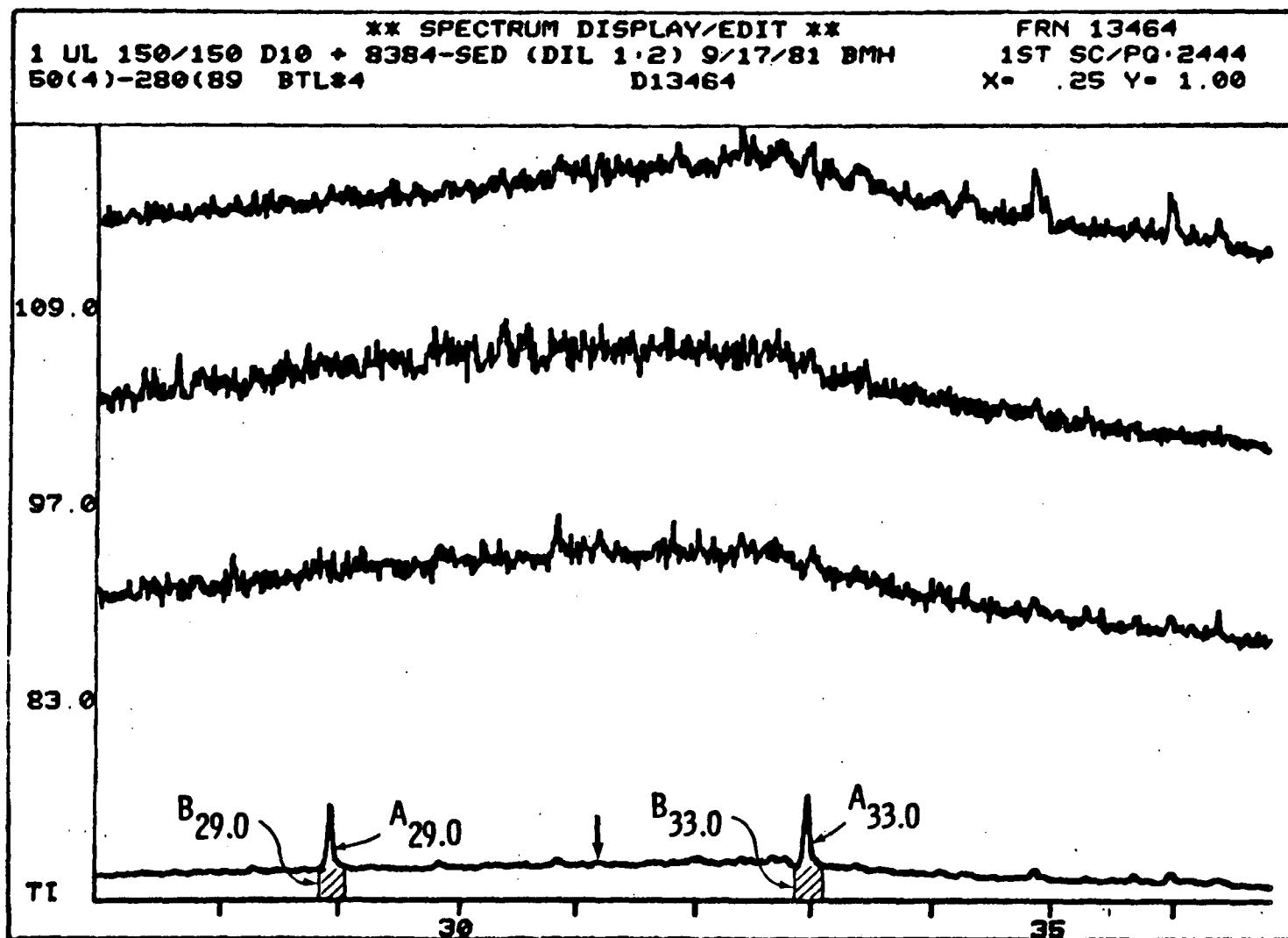


Figure C.11-10. Total ion chromatogram and selected ion chromatograms obtained from the analysis of the sediment extract from Plant B126S.

C.11-18

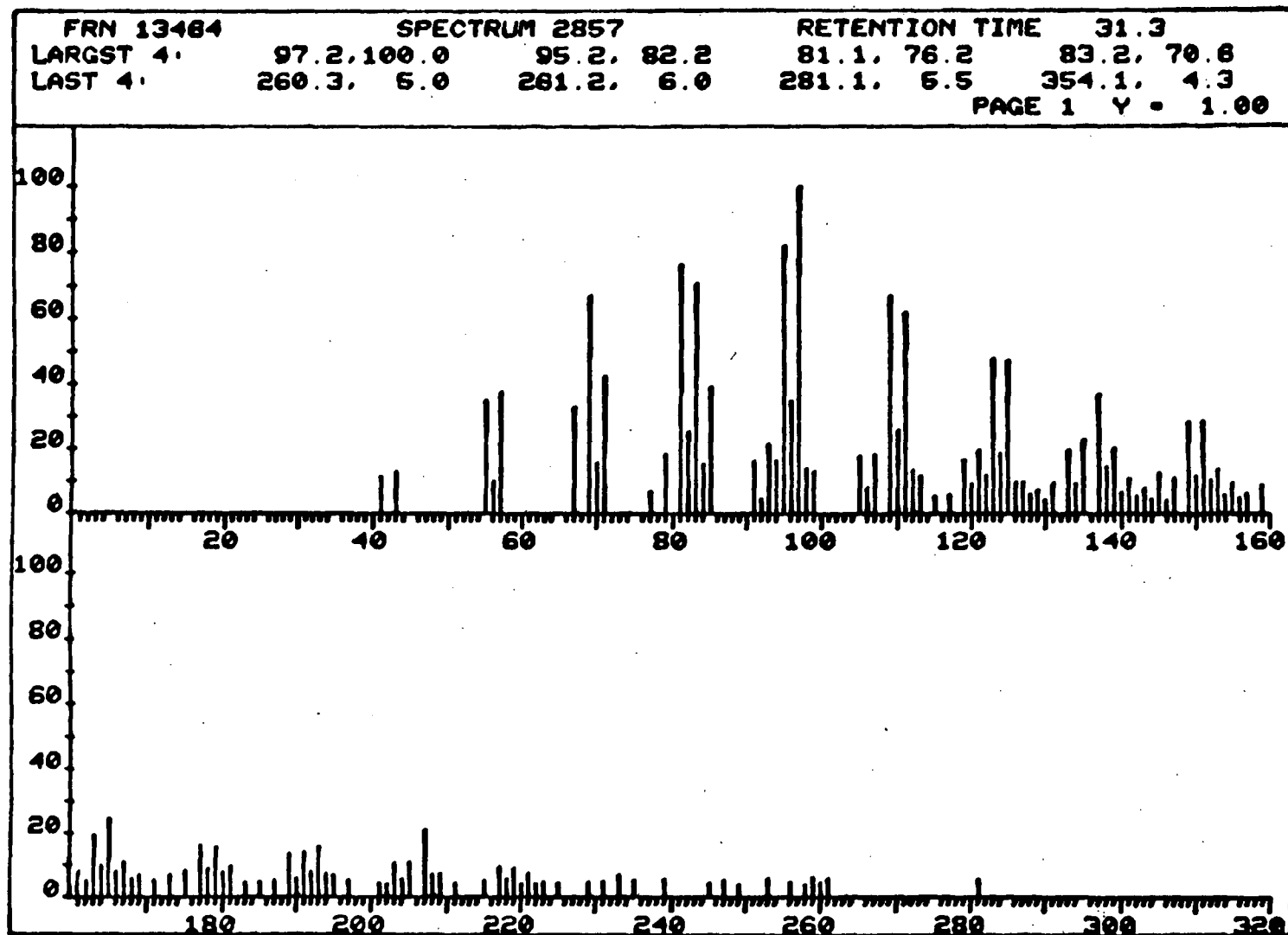


Figure C.11-11. Mass spectrum obtained at the retention time shown by the arrow in Figure C.11-10.

spectra taken of compounds eluting as discrete peaks on the broadly eluting peak will also contain spectra similar to that shown in Figure C.11-1. Figure C.11-9 is an example of this phenomenon. Table D.1-5 in Appendix D gives results for the base/neutral extract of the Plant A109 effluent. This unknown compound gives mass 216 as a possible molecular ion and also lists the other major ions present in the spectrum. However, most of the ions listed are due to the broadly eluting hump rather than the compound of interest. Due to the lack of time and funds for a more complete analysis, no attempt was made to determine which of the major ions present in the spectrum of coeluting components were due to the discrete component measured by the BATCH Quantifying program.

Figure C.11-10 also demonstrates a major difference in the method of quantification of capillary gas chromatographic/mass spectrometric data and capillary gas chromatographic/flame ionization detector data. The quantification of mass spectral data given in tables of Appendix D and E are the results of the Hewlett-Packard BATCH program. This program attempts to determine peak areas of discretely-chromatographable components such as those shown eluting at 29.0 and 33.0 minutes in Figure C.11-10. The areas measured automatically are those shown in the figure. However, the shaded areas below each of the two peak are not measured in the BATCH program and should not be measured if the area of the discretely eluting compound is of interest. However, the values of TCO and TCG, measured with capillary chromatography/flame ionization detection, measures the total area of eluting components which cause a response above a baseline value. For the times corresponding to the elution of the components at 29.0 and 33.0 minutes, the total areas measured in the TCO and TCG analysis include $A_{29.0}$ and $A_{33.0}$ plus $B_{29.0}$ and $B_{33.0}$. In addition, the total area of the broadly eluting hump is also included in the TCO and TCG analysis, but is not included in any of the areas of discretely-chromatographable component areas measured from mass

spectral data. This very important difference in quantitation explains major differences which occur between the TCO and TCG values determined with flame ionization detection and the sum of components measured from capillary chromatographic/mass spectrometric data. Although a greater level of confidence can be placed on the accuracy of some "tentative" identifications than of others, there is no way to quantify this; consequently, many unknowns for which no standards have been analyzed are given tentative identifications.

C.11.4 Quantitation of GC/MS Data

The calculations used for determining the concentration of organics in sample extracts were performed in two ways. All levels of deuterated spiking compounds were determined using the response of the molecular ion of each of the compounds, relative to the anthracene-d₁₀ molecular ion. Therefore, all recovery data were calculated using authentic standards.

The amounts of all other compounds were determined assuming the total ion response of each compound to be equal to the response of the anthracene-d₁₀ internal standard. This latter calculation was made using the following relationship:

$$\text{Concentration of X} = \text{concentration Anthracene-d}_{10} \frac{\text{Total ion area X in unknown}}{\text{Total ion area anthracene-d}_{10}} \times (\text{sample concentration factor})$$

The sample concentration factor takes into account the extraction and concentration of the 10-liter sample to a 10-mL extract or the extraction of 30 g sediment and final volume of 5 or 10 mL in the sediment extract. None of these data were corrected for recovery of the deuterated spike compounds.

C.11-5. QA/QC for Extractable Organics

In Phase II, MRC developed a routine procedure for assessing the condition of the mass spectrometer and the column in the gas

chromatograph. The mass spectrometer was tuned approximately once a week using perfluorotributylamine (PFTBA) which is the basis for the Hewlett-Packard AUTOTUNE program. The output from an average tune is shown in Figure C.11-12.

Samples were run in the automated BATCH ACQUIRE mode overnight, and with each batch of samples a system performance standard was analyzed. This included the compound decafluorotriphenylphosphine (DFTPP) which was analyzed by the Hewlett-Packard program: DFTPP EPA Criterion Verifier. The output from a typical analysis by this program is shown in Figure C.11-13. If masses other than 51 and 127 fell outside the ranges for the DFTPP spectrum, the tuning of the mass spectrometer was re-examined.

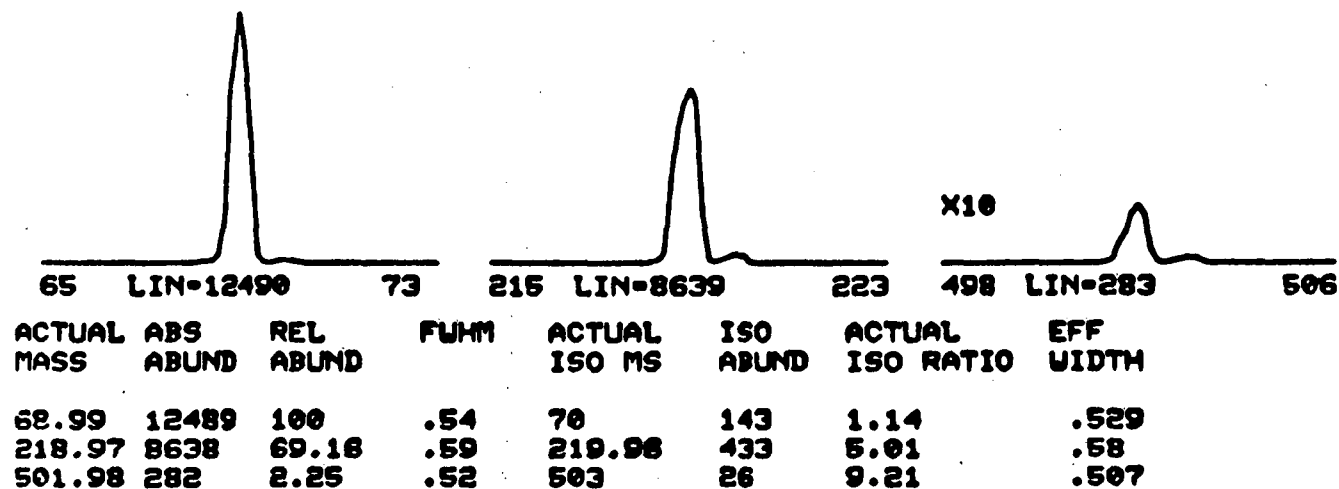
Typically, the m/e 51 and 127 on our instrument fell somewhat below the normal range specified by the program. This is because the DFTPP criteria were designed for and tested on Finnigan mass spectrometers, which use DFTPP as their tuning compound. The Finnigan mass spectrometers are typically tuned to optimize sensitivity in the lower mass region. The Hewlett-Packard autotune program, which tunes to PFTBA, optimizes sensitivity for higher mass ions (m/e 219 and 502). This deviation from the DFTPP criteria poses very little problem in terms of data interpretation, once one is aware that intensities of the lower masses should not be expected to be as high as in the library spectra. The higher abundances of high mass ions often facilitates interpretation since the lower masses are common to a wider variety of compounds.

The substances present in the system performance standard were: (1) 2,6-dimethylphenol, (2) 2,6-dimethylaniline, (3) decanol, (4) pentachlorophenol, (5) anthracene-d₁₀ added prior to analysis, (6) octadecene, (7) octadecane, (8) DFTPP, (9) eicosane, (10) heneicosane, (11) pyrene, (12) methyl stearate, and (13) chrysene. Figure C.11-14 shows a typical chromatogram obtained from

Y CURRENT PARAMETERS *

L05985-10041HJ

DATE (FRN 1000) : 1/26/81 1:15
 REPELLER(V)=10.84 EM VOLTAGE(V)=2200
 DRAWOUT(V)=26.5 AMU GAIN=115
 ION FOCUS(V)=35 AMU OFFSET=113
 ENT LENS(MV/AMU)=133 MASS AXIS GAIN=1.00157
 X-RAY(V)=154 MASS AXIS OFFSET=-.190491
 EMISSION(UA)=300 IONS: POSITIVE
 ELECT. ENERGY(EV)=70 ACTUAL SOURCE TEMP =200
 LOG AMP OFFSET=1



OPTION?

Figure C.11-12. A typical result from tuning the Hewlett-Packard 5985 mass spectrometer with PFTBA.

DFTPP EPA CRITERION VERIFIER

DRN: 22512
SPECTRUM: 2011

Mass	Rel. Abund.	Criterion
** 51	9.95206	30-60% MASS 198
68	0	< 2% MASS 69
69	29.7239	
70	0	< 2% MASS 69
** 127	33.4849	40-60% MASS 198
197	0	< 1% MASS 198
198	100	BASE PEAK
199	6.59613	5-9% MASS 198
275	22.6732	10-30% MASS 198
365	1.70276	> 1% MASS 198
441	14.7049	< MASS 443
442	73.8387	> 40% MASS 198
443	16.0357	17-23% MASS 442

NOTE: '**' indicates out of range!

PRESS <RETURN> TO RERUN...

Figure C.11-13. Computer analysis of mass spectrum of DFTPP.

** SPECTRUM DISPLAY/EDIT **
1 UL 20/80 D10 + COL.PERF.STD. 4/10/81 BMH 30m FS SE-541ST SC/PQ: 610
50(4)-280(8) BTL*12 D22512 X= .25 Y= 1.00

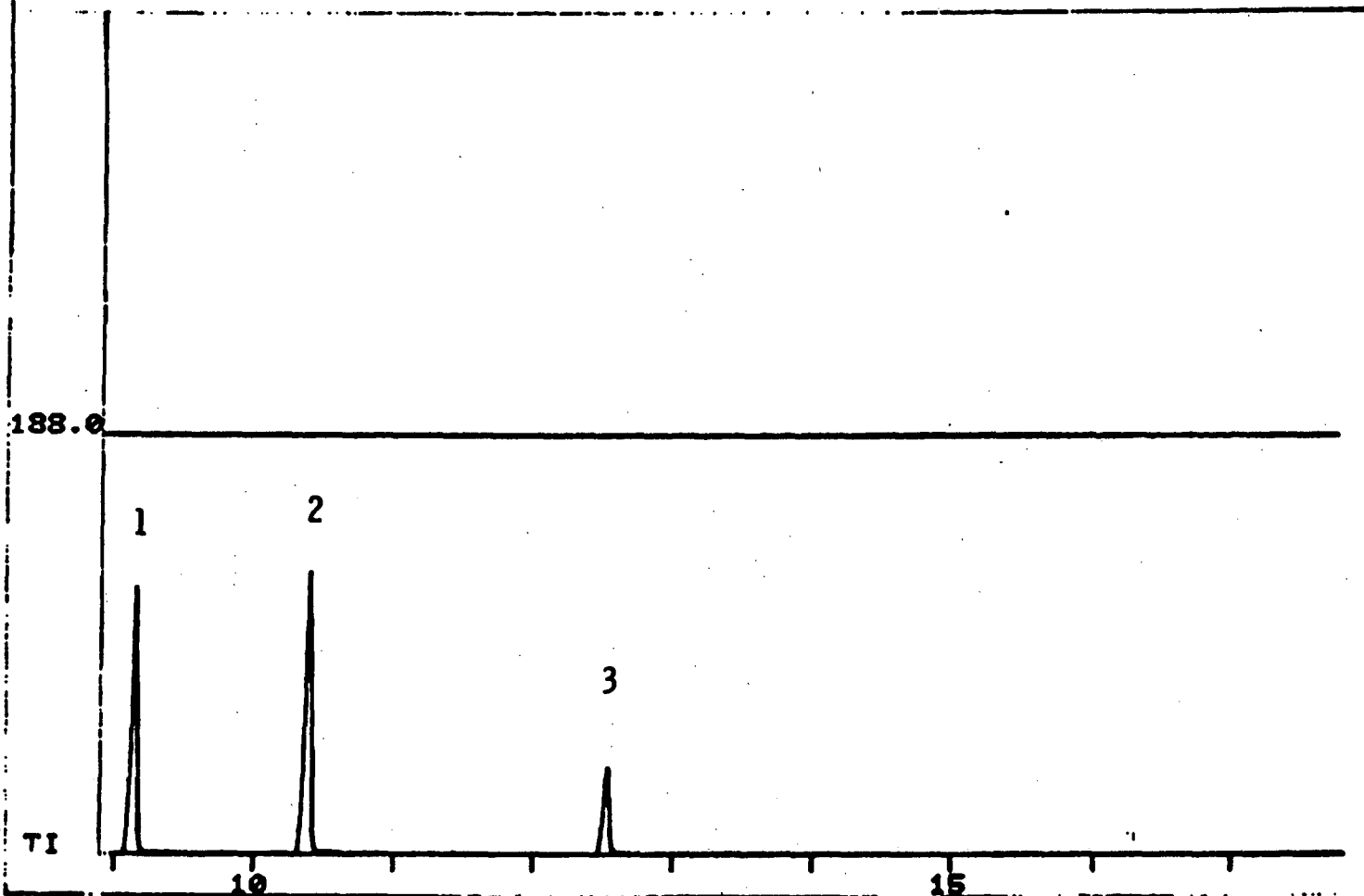


Figure C.11-14. Chromatogram of the column performance standard with the GC column in average condition. The numbered peaks are identified in the text.

C.11-24

** SPECTRUM DISPLAY/EDIT **
 1 UL 20/80 D10 + COL.PERF.STD. 4/10/81 BMH 30m FS SE-541ST SC/PG:1535
 53(4)-280(8) BTL*12 D22512 X= .25 Y= 1.00

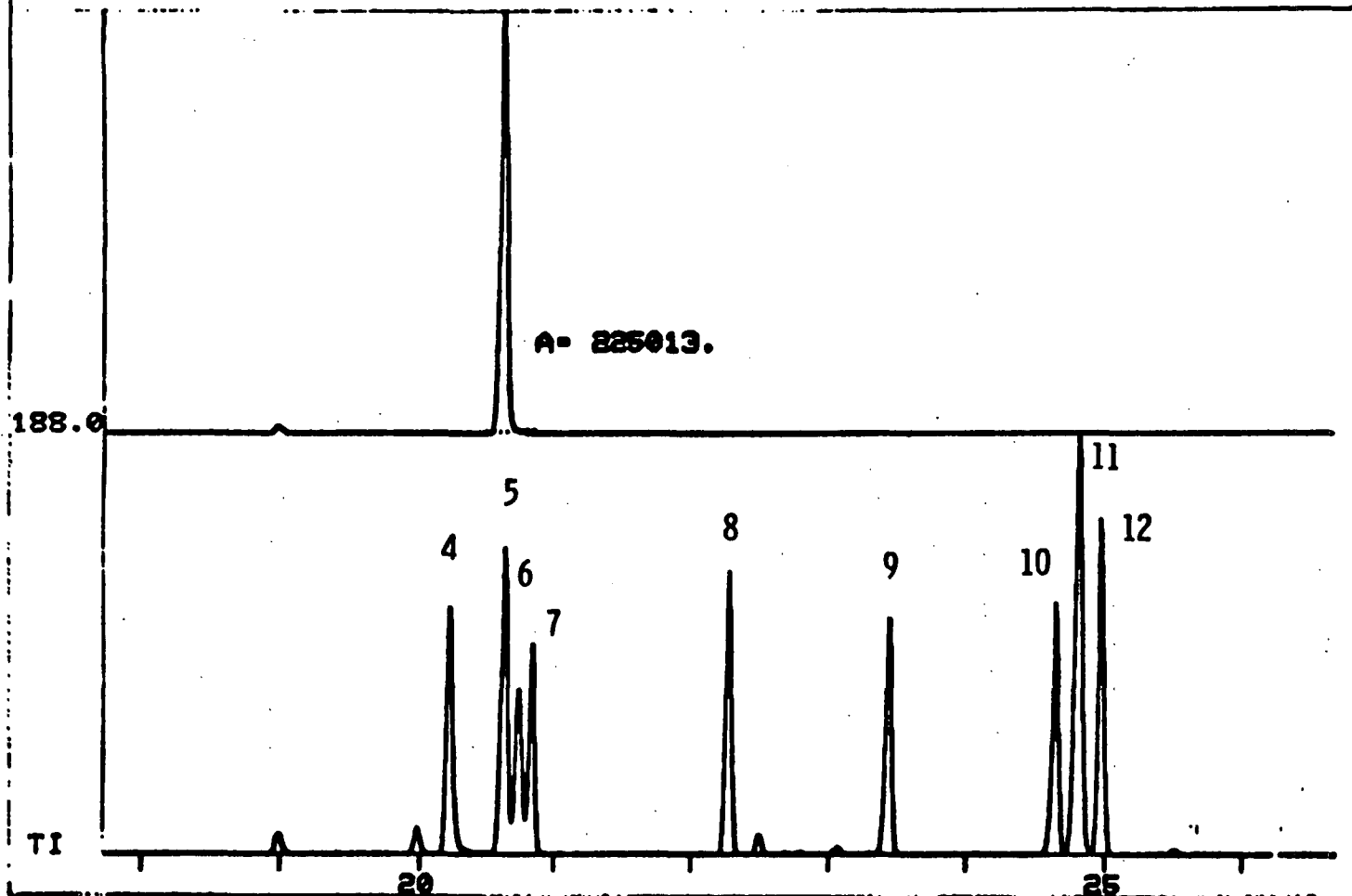
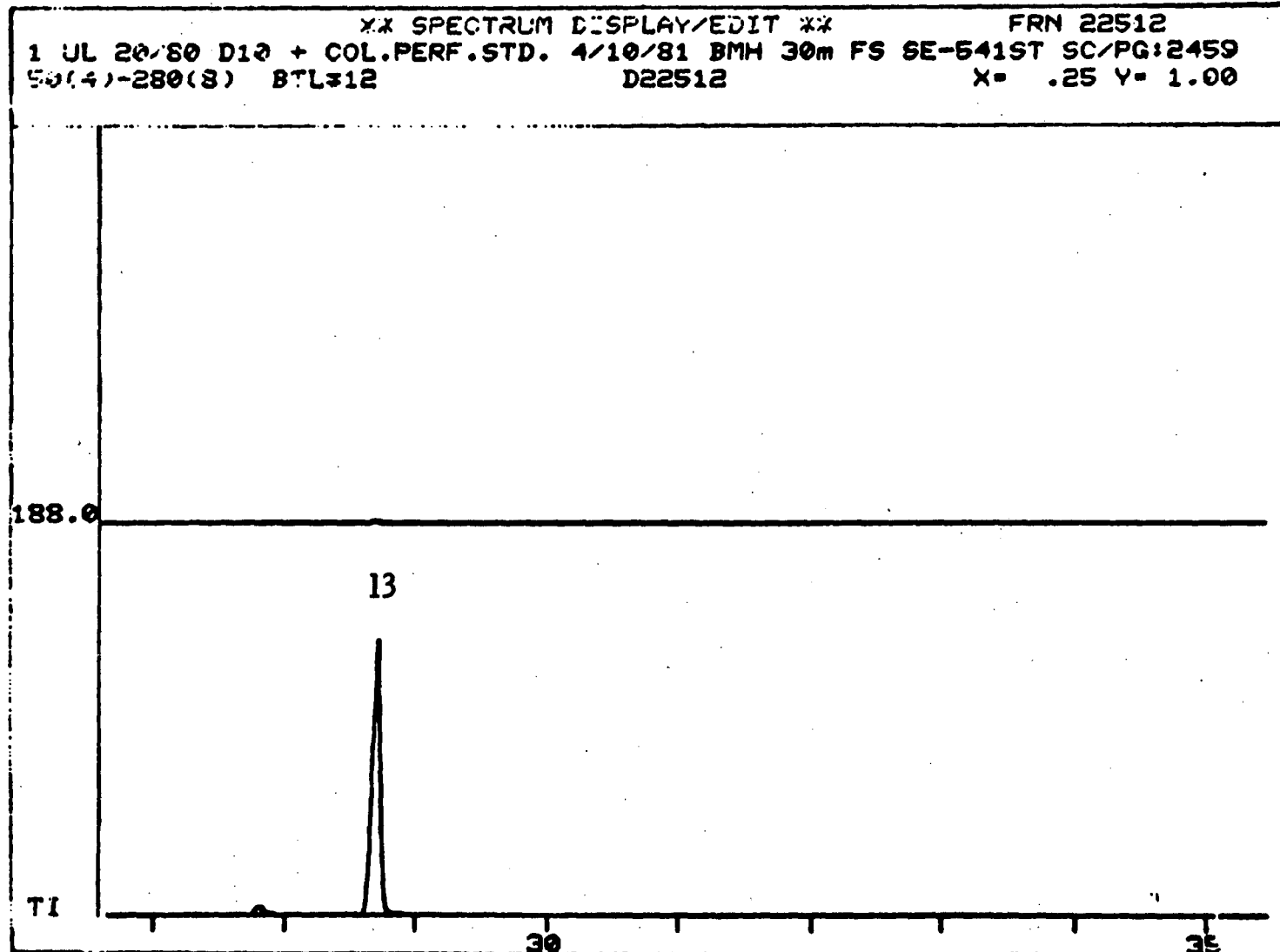


Figure C.11-14 (continued)

C.11-25



C.11-26

Figure C.11-14 (continued)

the standard. By examining the resolution of the peaks ~20.7 min and ~24.7 min, and by looking at the tailing of certain peaks such as decanol and pentachlorophenol, we visually determined the condition of the column. When the resolution and tailing were substantially worse than in a new column, the injection port insert was replaced and the front end of the column was broken off or the column replaced.

In Phase II, to evaluate the reproducibility of quantitation using the BATCH mode for determining peak areas on an actual sample, the unfractionated acid extract from B142S was analyzed 3 times (by placing portions of the sample plus the anthracene-d₁₀ internal standard in 3 vials in the autosampler). Taking the mean and the percent deviation from the mean of the areas of 30 peaks identified by the BATCH ROUTINE in all 3 samples, it was found that the average percent deviation was $\pm 21\%$. It was also observed that the percent deviations from the mean for 8 of these peaks were substantially above 21%.

For these peaks the chromatograms were re-examined manually, and it was apparent that due to the complexity of the sample, i.e., overlapping peaks, the computer routine had not correctly identified the areas to be measured. When they were measured manually, the average percent deviation from the mean for these 8 peaks amounted to 10%. Thus, the deviation one should expect on area replications by automated peak quantitation routines is approximately 20%, with greater reproducibility possible if manual analysis is warranted. During Phase III, the output of the BATCH peak detection program was visually compared with the total ion chromatogram and where relative peak areas did not agree with relative peak heights, the areas of the peaks in question were measured manually.

To evaluate the linearity of instrument response, a sample containing indene was serially diluted, each time, by a factor of 2

from 292 mg/L to 0.142 mg/L, and the samples were analyzed in the standard fashion using BATCH mode. A least-squares line was calculated for the actual concentration vs. the total ion area of the indene peak divided by the m/e 188 area from anthracene-d₁₀ internal standard (the method always used to compensate for instrument variations). This gave a slope of 0.0245, an intercept of 0.0721, and a correlation coefficient of 0.998.

The difference between the true concentration at each measurement and the concentration calculated using the measured area and the least-squares line was obtained. The mean difference was 4.5 mg/L, and the mean percent difference was 58%.

This large percent difference reflects the increase in inaccuracy, when expressed on a percentage basis, at the low concentration end of the analysis. If one considers only the points with concentrations from 2 mg/L to 292 mg/L, the mean percent difference is 28%.

In order to assess the accuracy of GC/MS quantitation, two standards were compared with each other. A Supelco phenols standard was analyzed on 8 February 1981, and a freshly prepared MRC standard containing many of the same phenols was analyzed on 4 April 1981. In both standards the concentrations of the components were close to 100 mg/L. Taking the concentrations in the MRC standard to be correct, the concentrations of the components in the Supelco standard were calculated and compared with their stated values. The substances analyzed included 2-nitrophenol, 2,4-dinitrophenol, 2,4-dichlorophenol, 4-chloro-*m*-cresol, 2,4,6-trichlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-*o*-cresol, and pentachlorophenol.

Based on MRC standards the average percent deviation of the values found from the stated values was 28%, excluding 4-nitrophenol, where 7 mg/L was found vs. the stated 100 mg/L.

The quantitation of 4-nitrophenol has been a source of difficulty previously, as it appears to diminish in concentration with storage time of the standard. The indication from the comparison of standards is that except for a particularly troublesome compound such as the 4-nitrophenol, the average uncertainty in the quantitation of clean samples in which the unknown component is of comparable concentration to the standard, is approximately $\pm 30\%$.

Finally, to show what one may expect for retention times of hydrocarbon, a standard consisting of normal alkanes from C_8 to C_{34} was analyzed following the usual procedures. The results are plotted in Figure C.11-15, where it is seen that the first normal alkane that can be identified by the MRC GC/MS analysis procedure is C_9 , b.p. 151°C , and the last one is C_{34} , b.p. $\sim 483^\circ\text{C}$. The linearity of elution time vs. boiling point is excellent up to C_{30} , at which time the oven temperature reaches its maximum, causing C_{32} and C_{34} to depart from the linear relationship.

C.11.6 Analysis of Standards

Three standard solutions were routinely analyzed along with effluent or sediment extracts in order to verify that good quality capillary chromatography and mass spectrometric analyses were being performed on sample extracts. In addition, capillary chromatographic/flame ionization detector system performance was also verified using the same set of standards analysis. Figure C.11-16 shows the total ion chromatogram obtained from the analysis of a benzene standard containing all acid priority pollutants; Figure C.11-17 shows the analysis of a benzene standard containing over 80% of the pesticide priority pollutants (excluding the Aroclor and toxaphene multicomponent priority pollutants). Figures C.11-19 through C.11-22 show capillary GC/FID chromatograms obtained from the analysis of the system performance standard, shown in Figure C.11-14, and the three

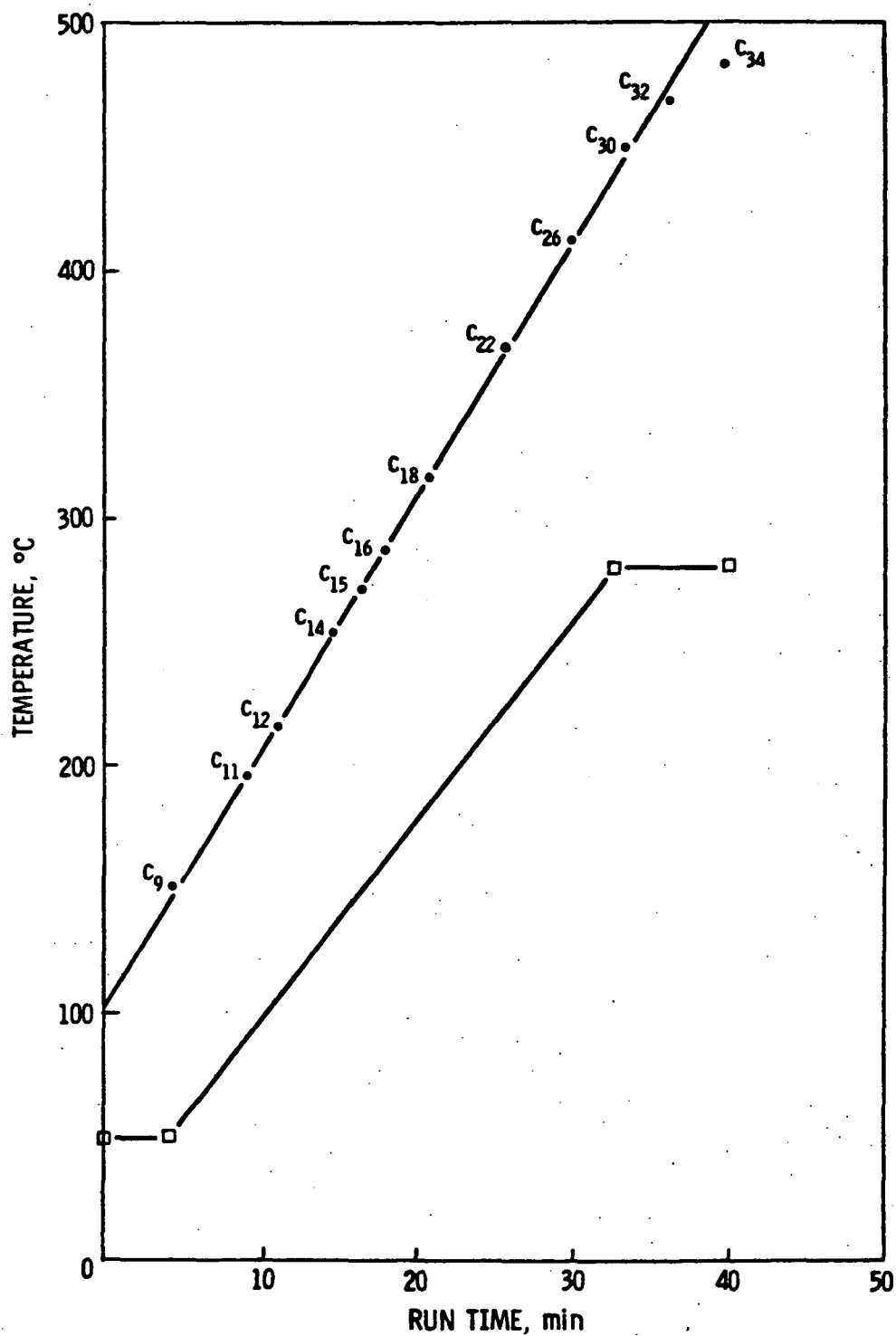


Figure C.11-15. Elution times for normal alkanes, C₉-C₃₄ in the GC/MS system. Upper curve: Boiling points of the alkanes indicated vs. retention time. Lower curve: GC oven temperature profile.

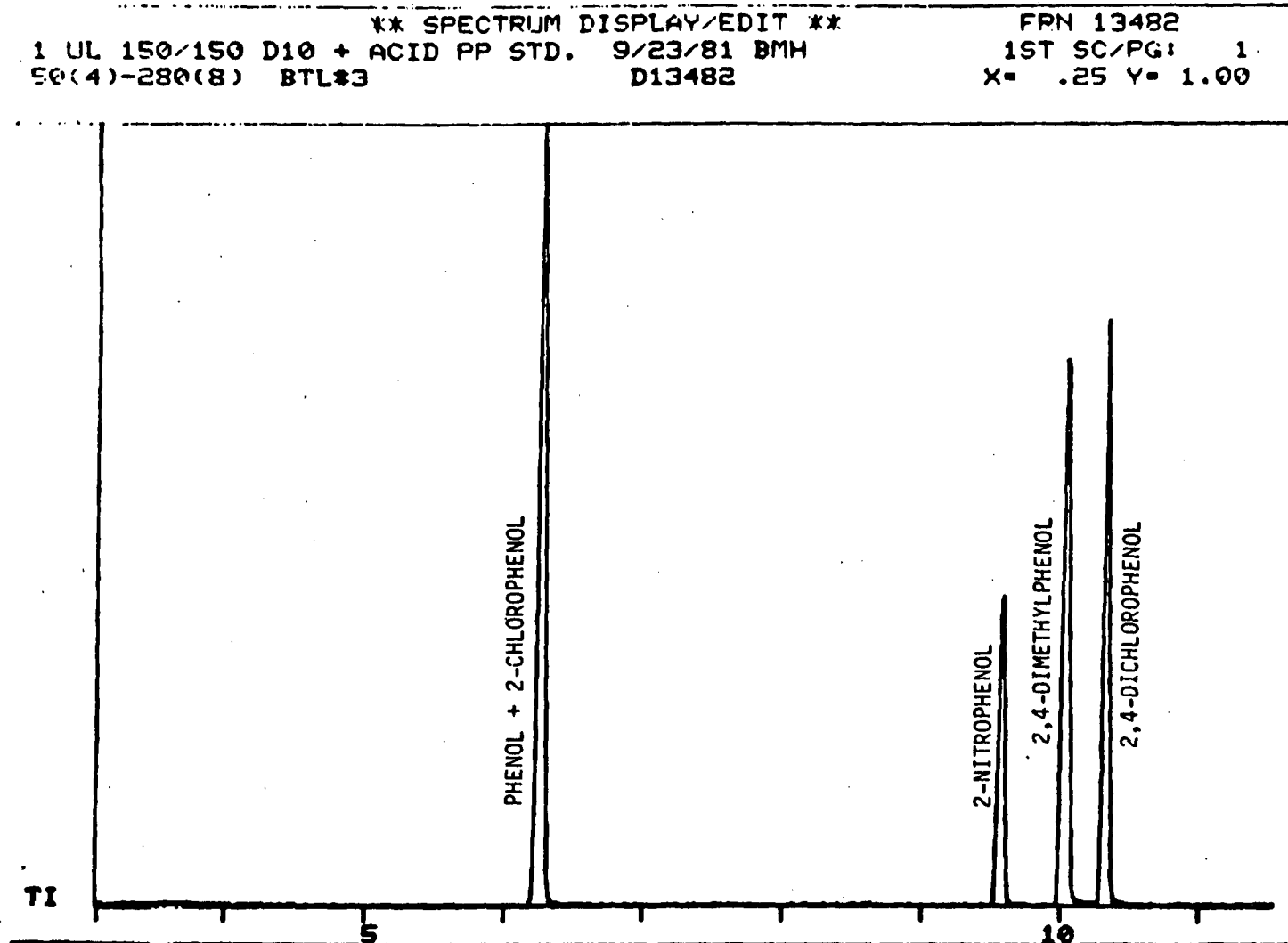


Figure C.11-16. Total ion chromatogram obtained from the analysis of a 200- $\mu\text{g/mL}$ component acid priority pollutant standard.

C.11-32

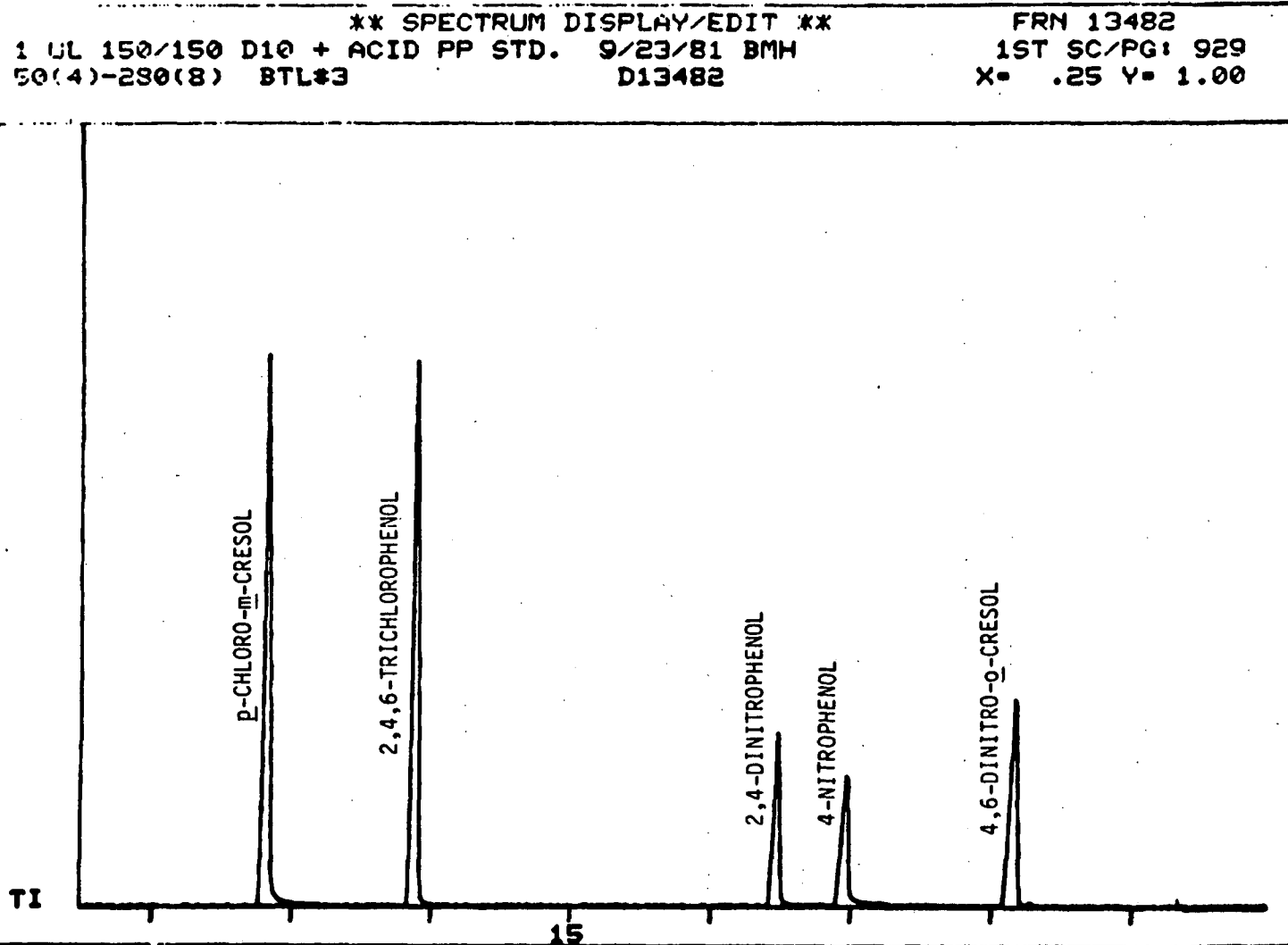


Figure C.11-16 (continued)

C.11-33

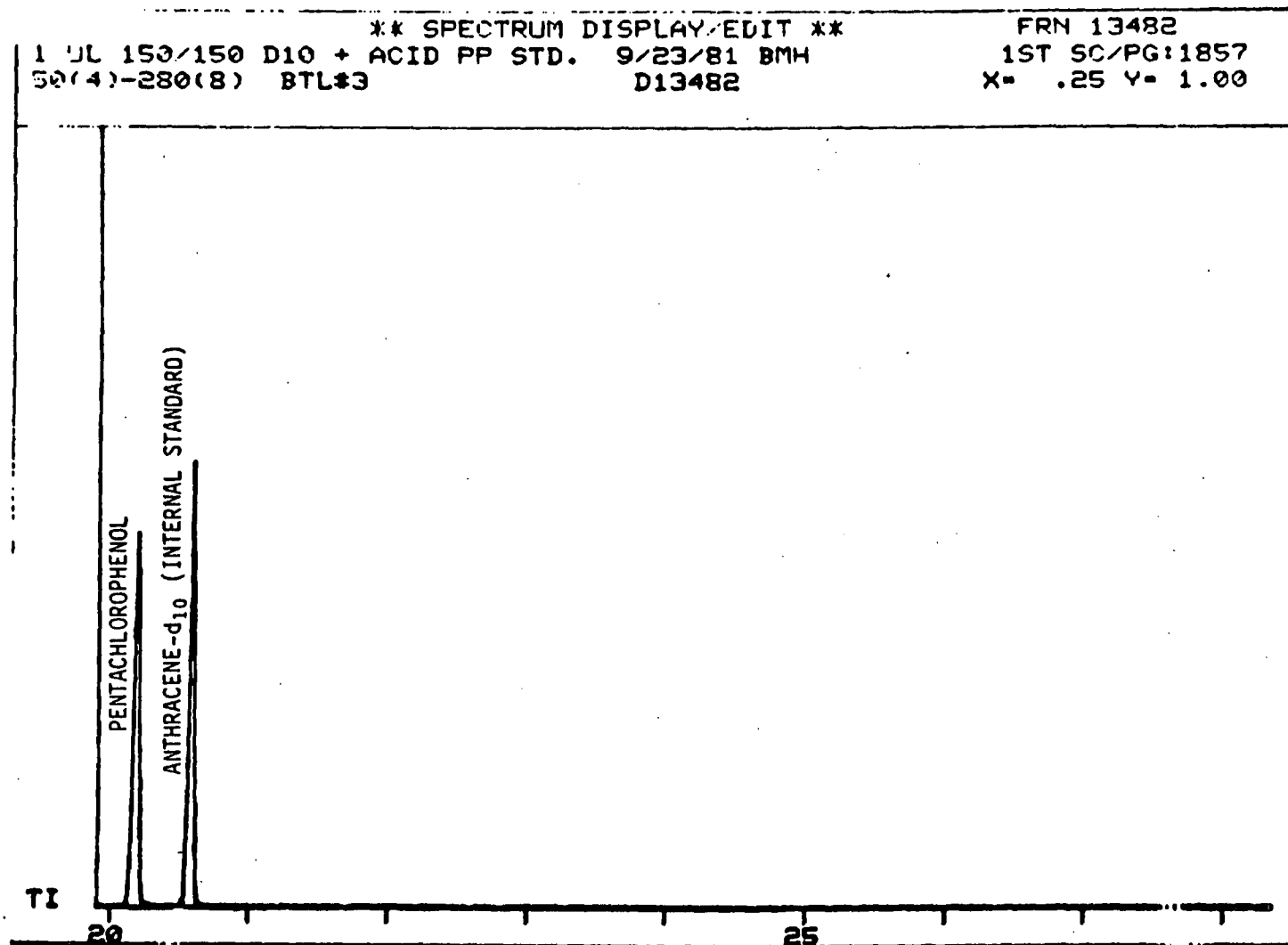


Figure C.11-16 (continued)

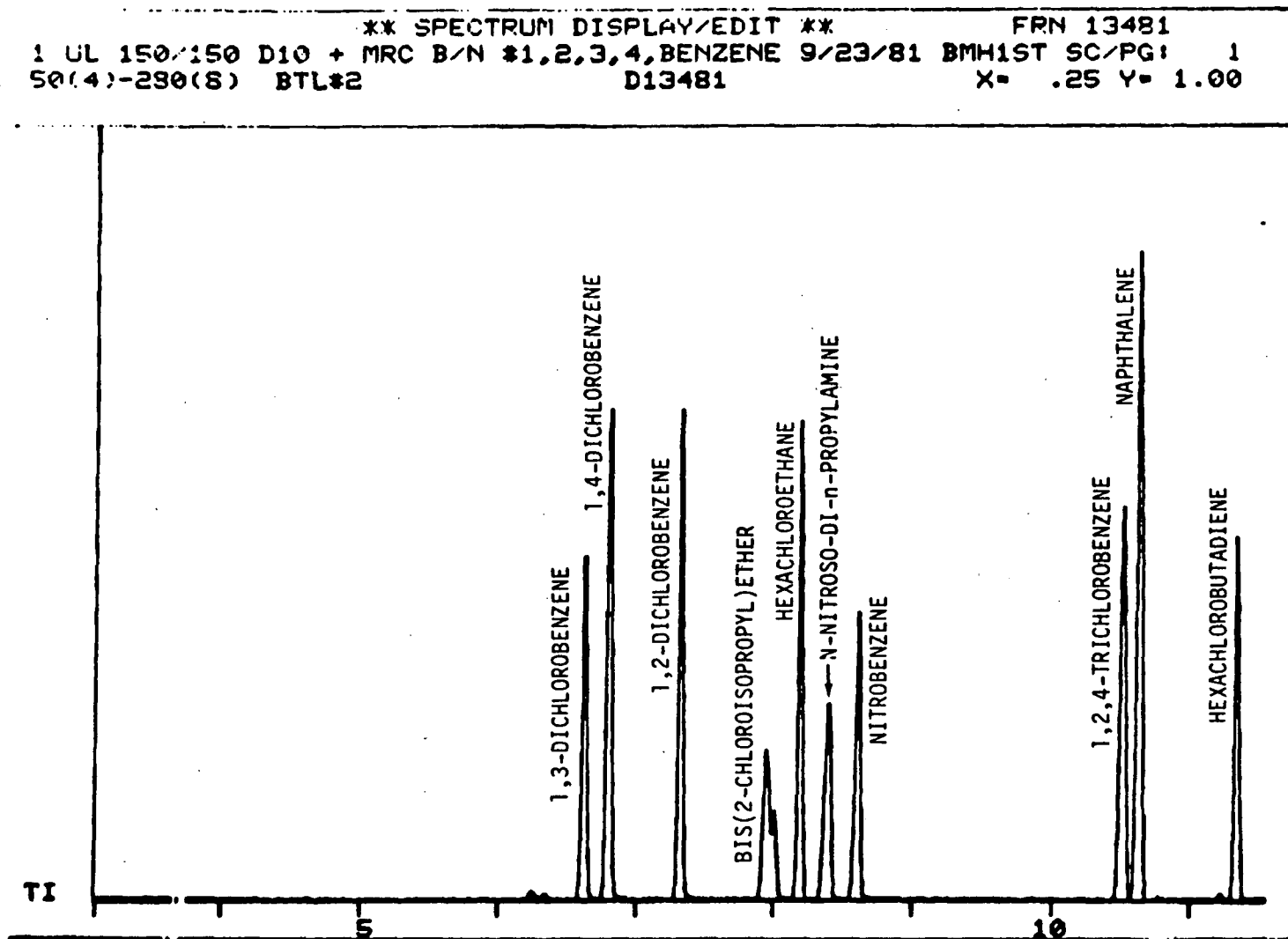


Figure C.11-17. Total ion chromatogram obtained from the analysis of a 100- μ g/mL component base/neutral priority pollutant standard.

C.11-35

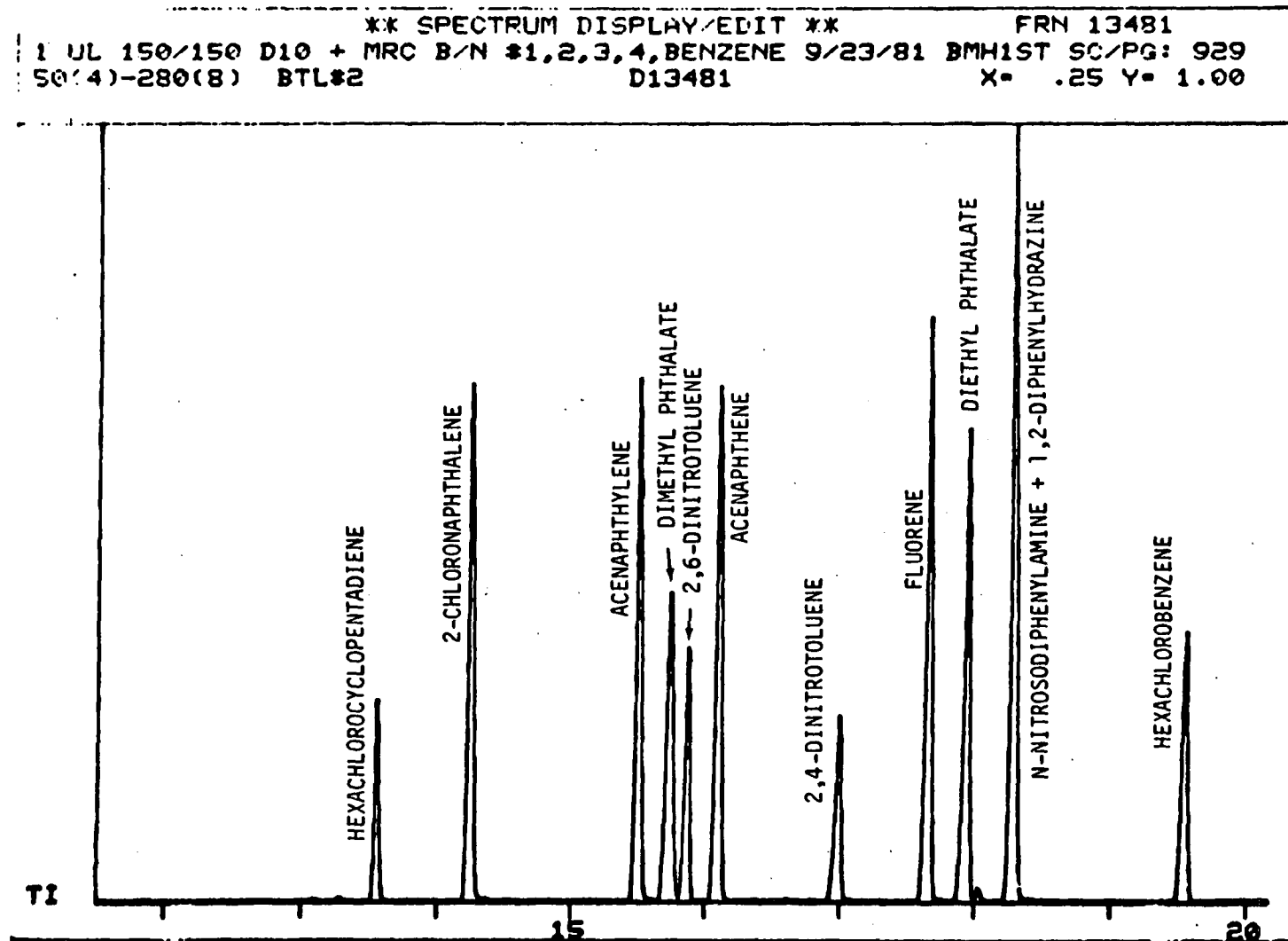


Figure C.11-17. (continued)

C.11-36

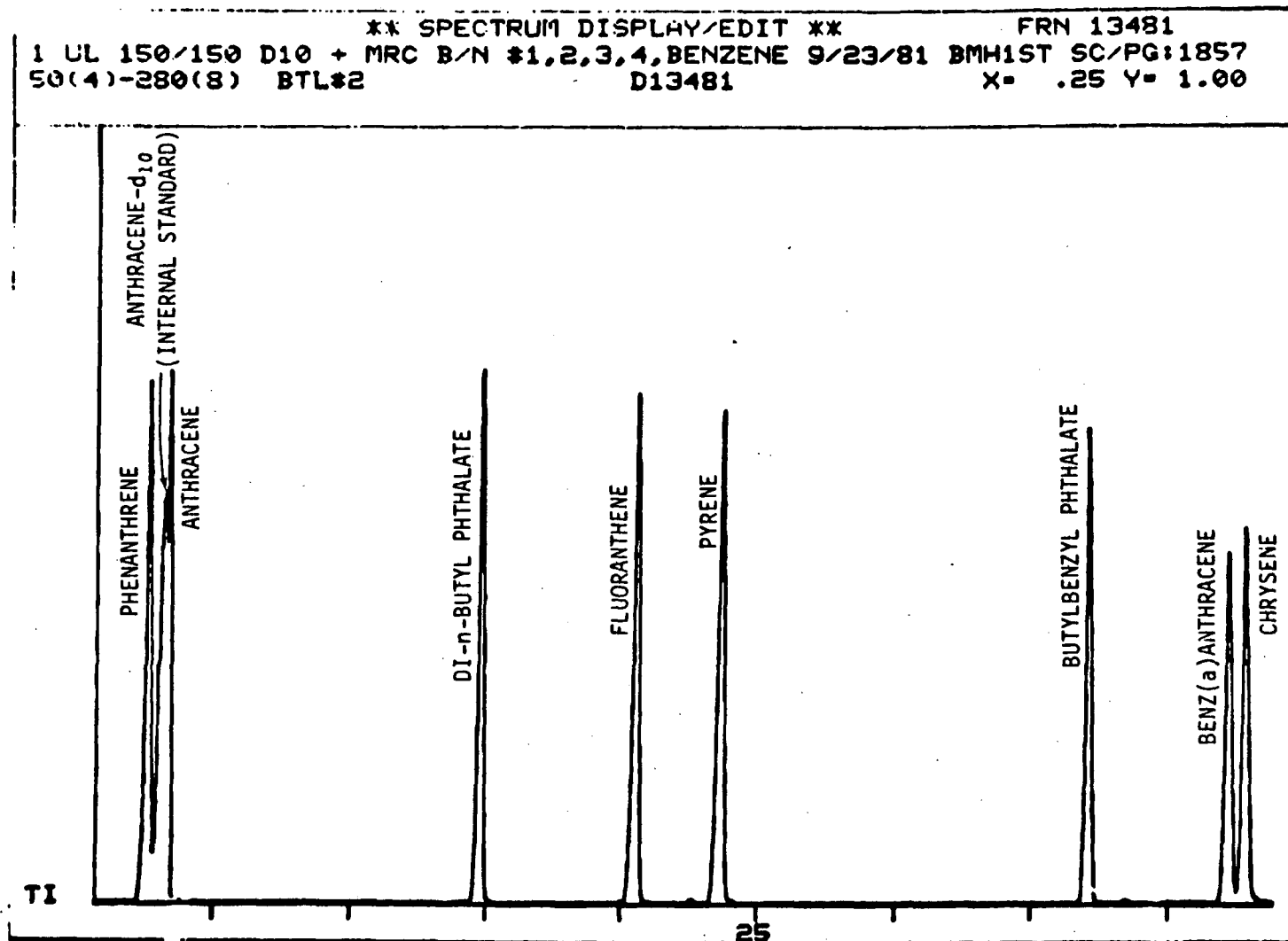


Figure C.11-17 (continued)

** SPECTRUM DISPLAY/EDIT **
1 UL 150/150 D10 + MRC B/N #1,2,3,4,BENZENE 9/23/81 BMH1ST SC/PG:2785
50(4)-280(8) BTL#2 D13481 X= .25 Y= 1.00

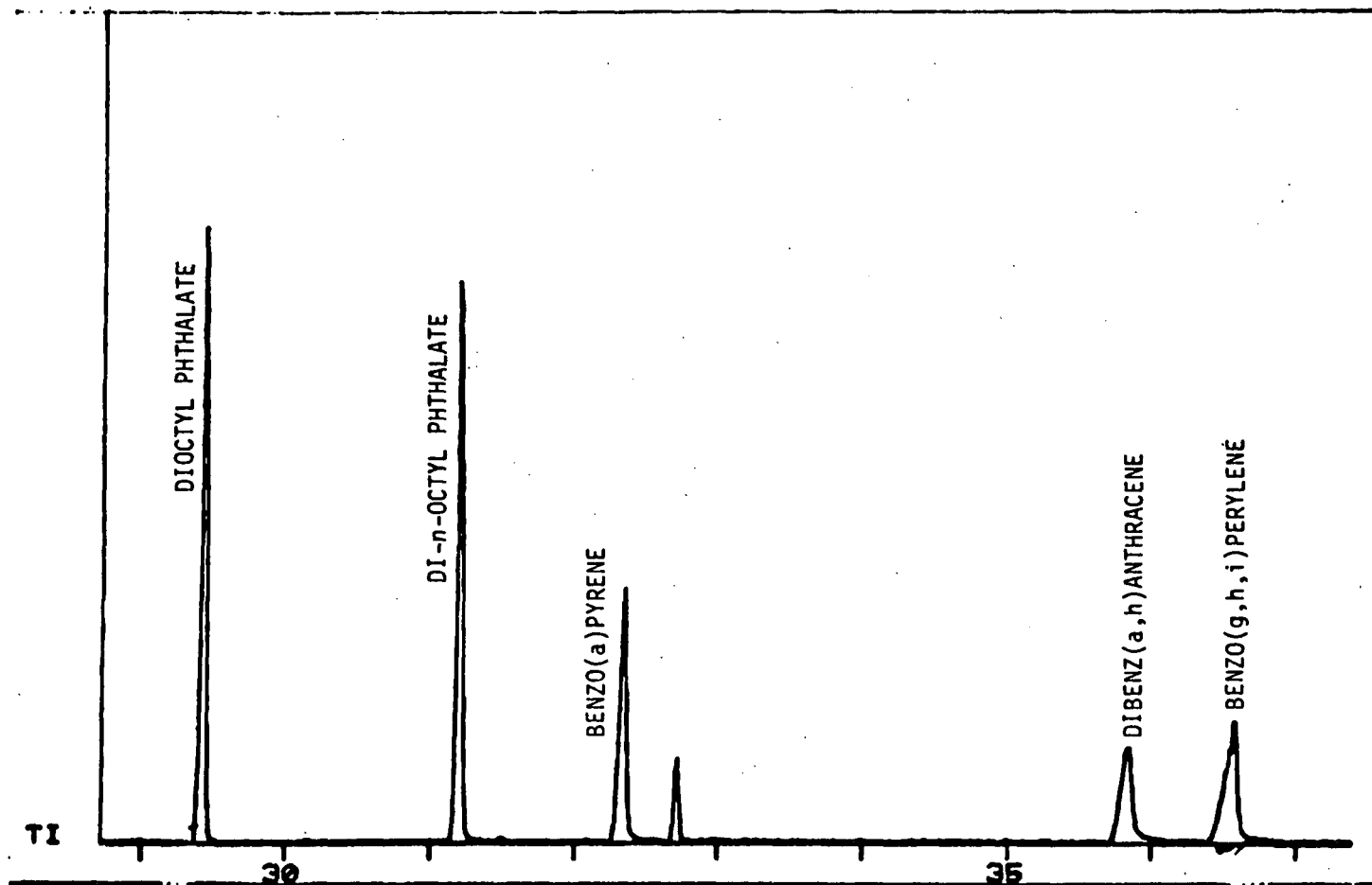


Figure C.11-17 (continued)

priority pollutant standards, shown in Figures C.11-16 through C.11-18. The identification of selected components is given in each of the above figures. As can be seen, excellent agreement was observed between the total ion chromatograms obtained from capillary GC/MS analyses and chromatograms obtained from capillary GC/FID analyses of these standards. Therefore, the correlation of data obtained from these two analytical techniques should exclude any differences between chromatography from these two analytical systems.

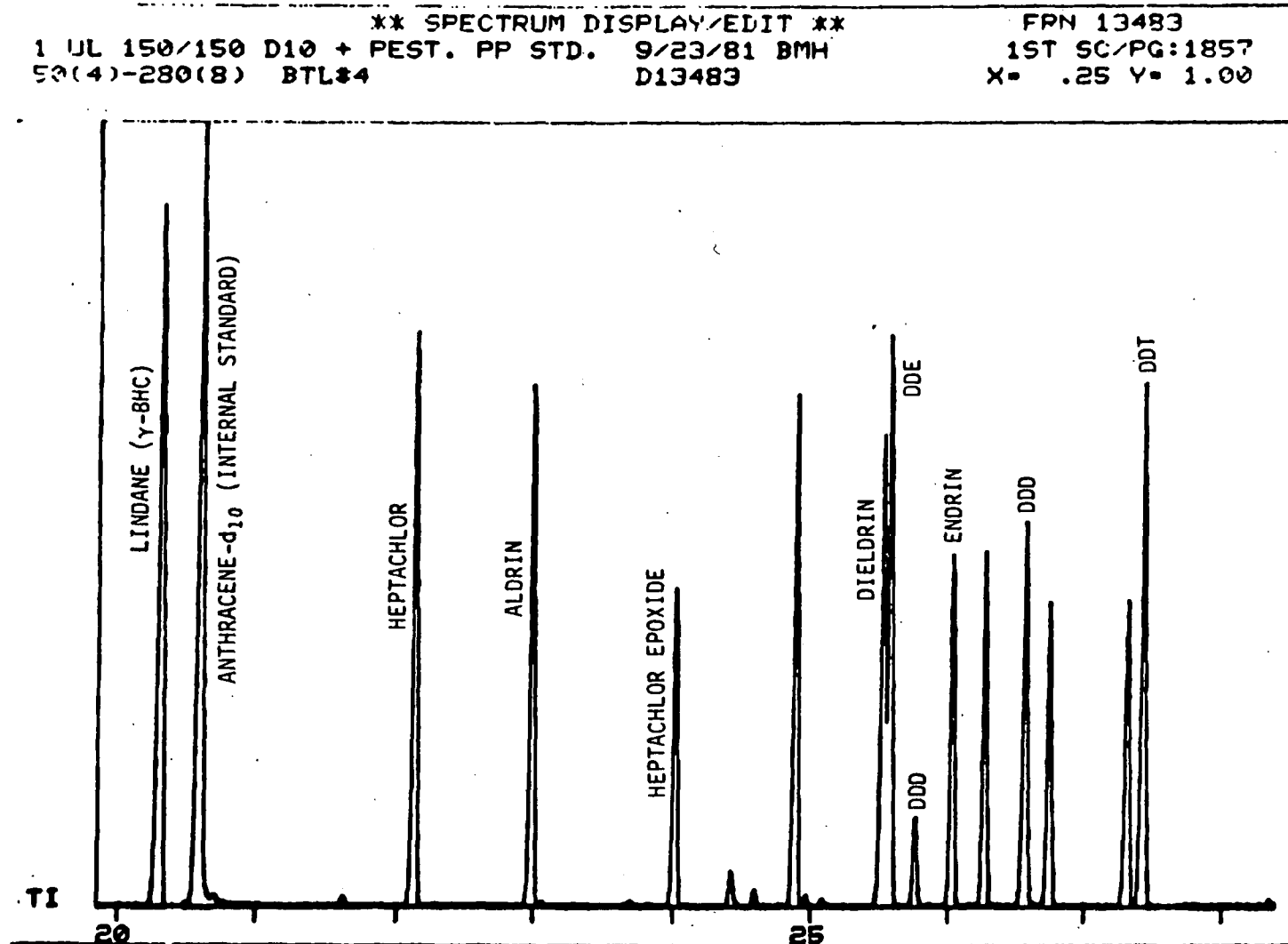


Figure C.11-18. Total ion chromatogram obtained from the analysis of a 100- μ g/mL component pesticide priority pollutant standard.

C.11-40

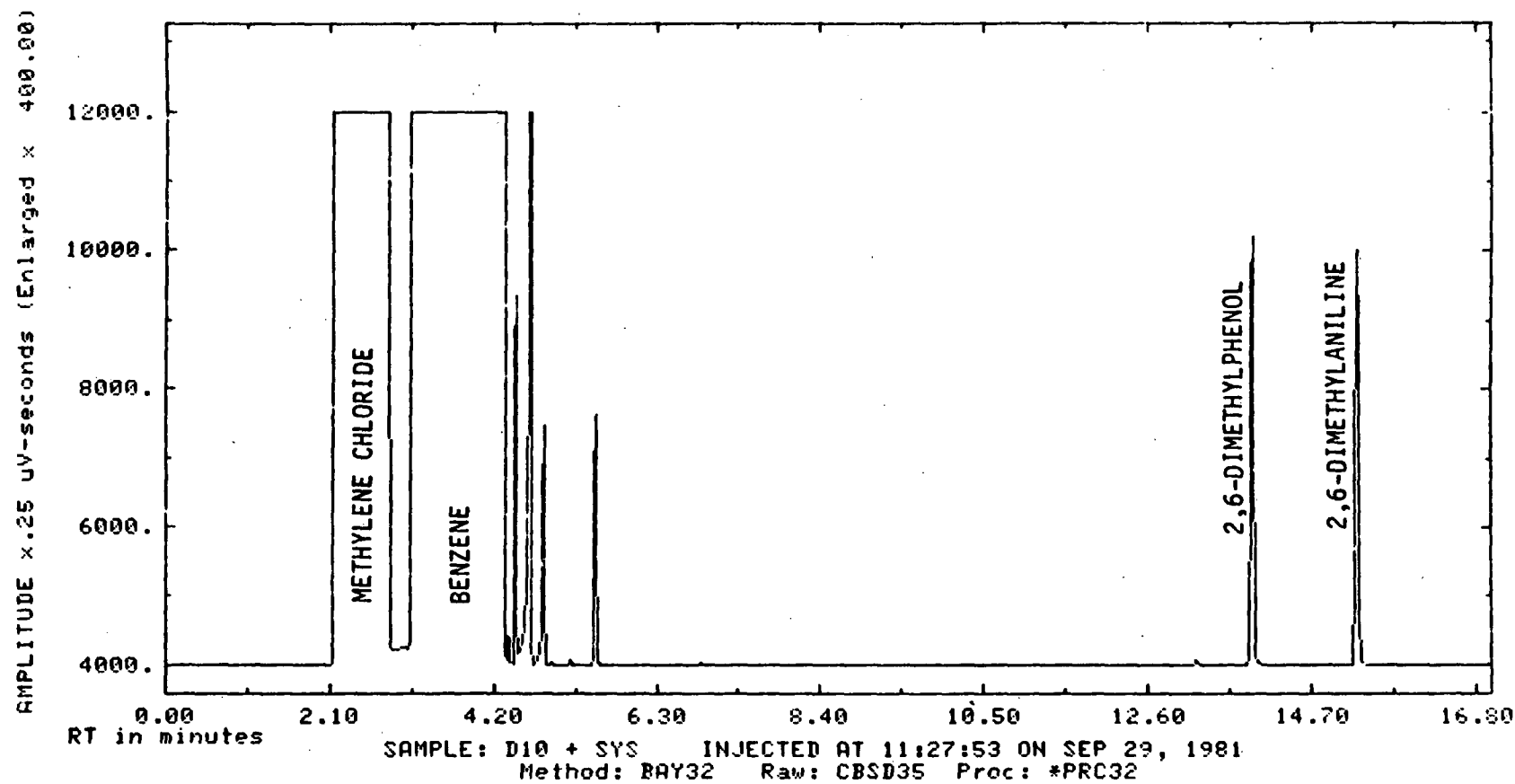


Figure C.11-19. FID chromatogram obtained from the capillary GC analysis of the system performance standard, shown analyzed in Figure C.11-14.

C.11-41

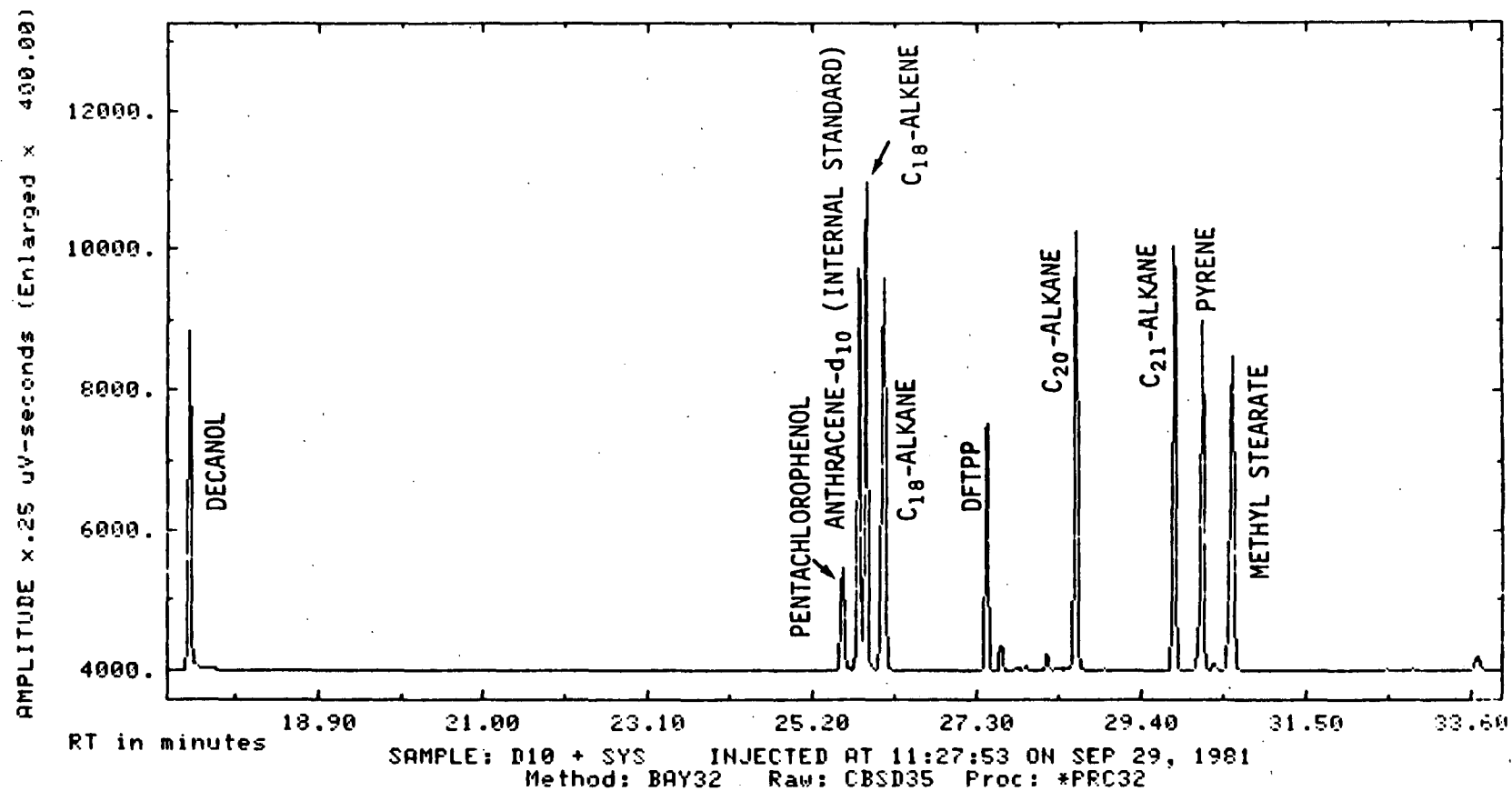


Figure C.11-19 (continued)

C.11-42

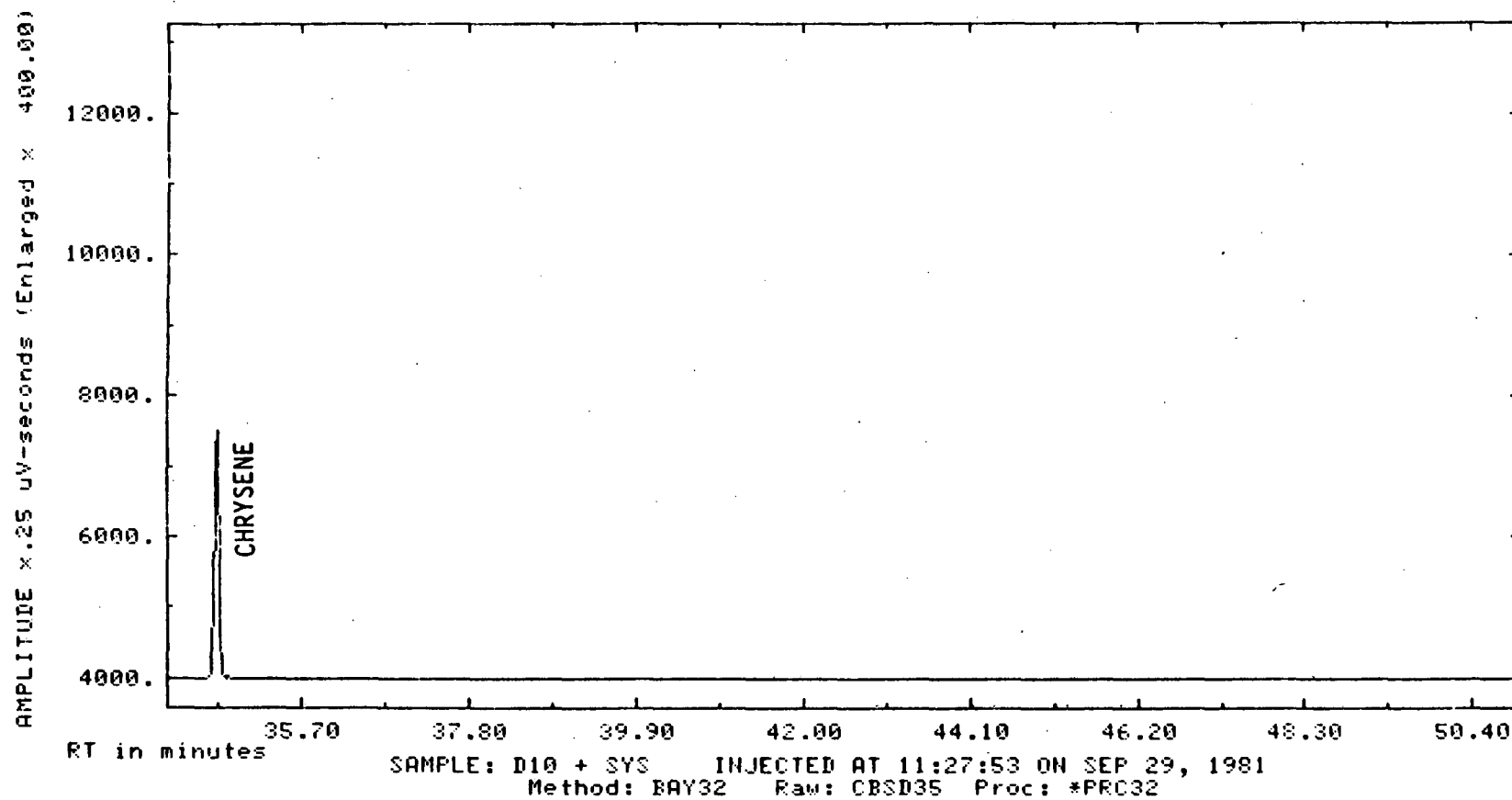


Figure C.11-19 (continued)

C.11-43

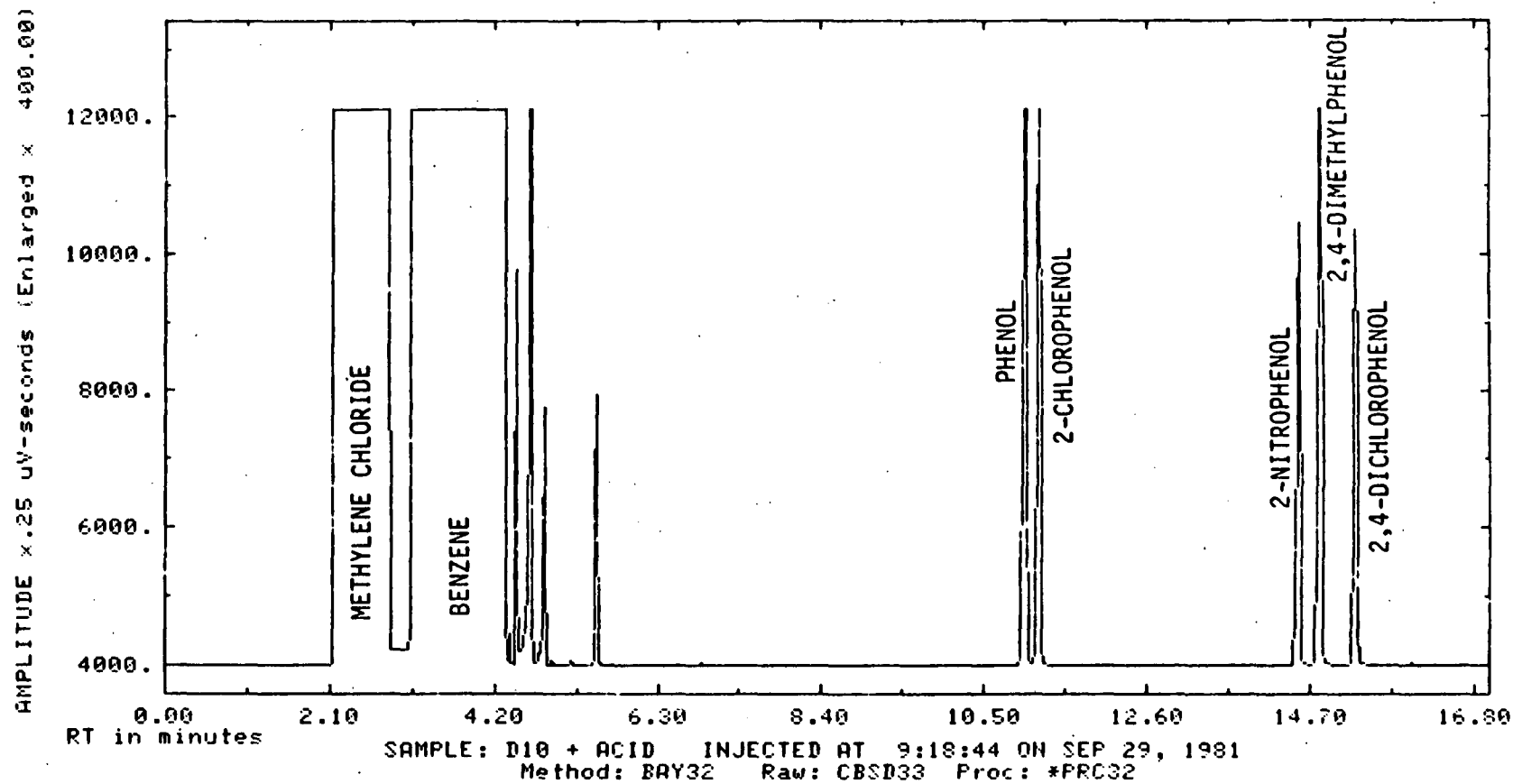


Figure C.11-20. FID chromatogram obtained from the capillary GC analysis of the acid priority pollutant standard, shown analyzed in Figure C.11-16.

C.11-44

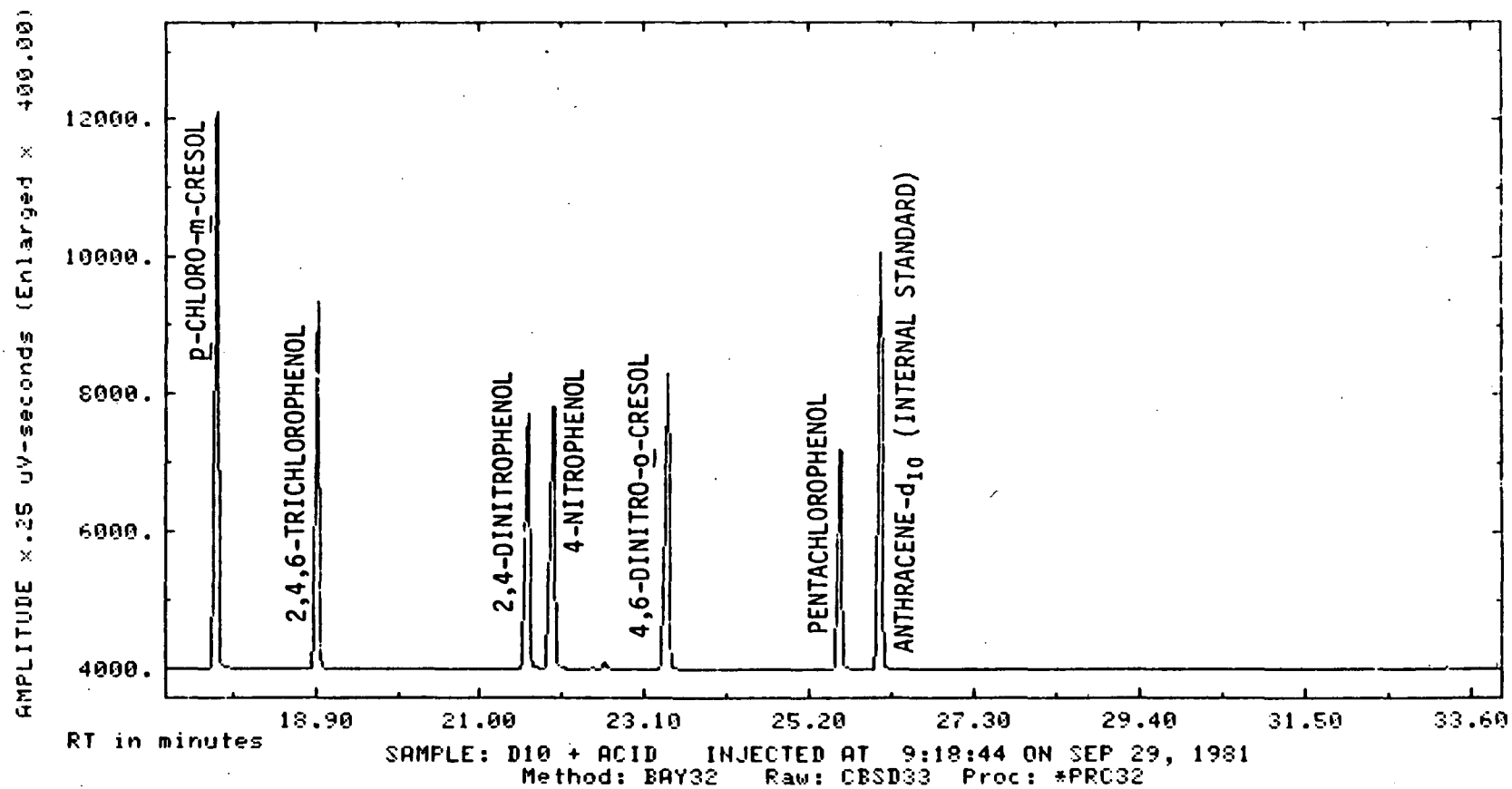


Figure C.11-20 (continued)

C.11-45

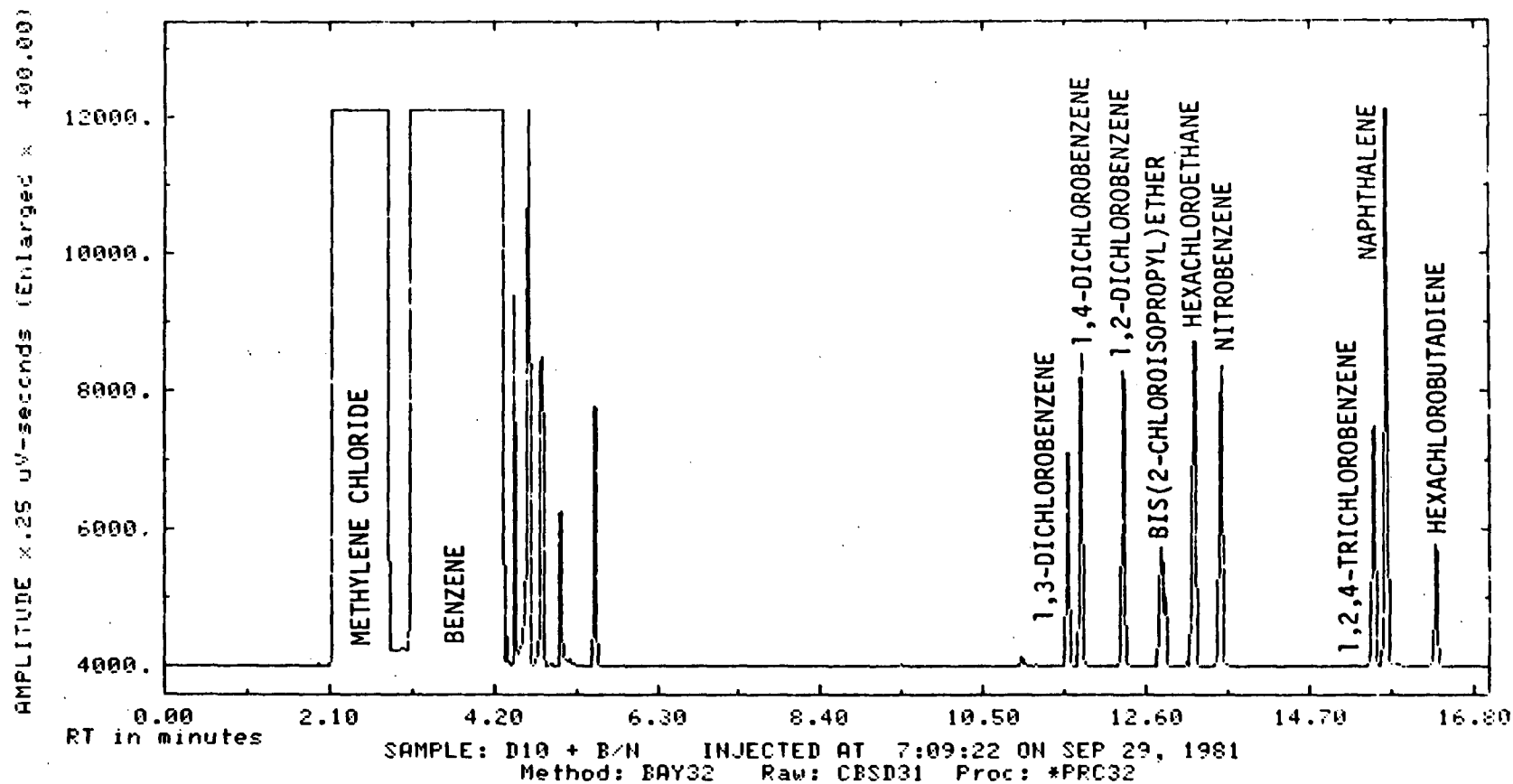


Figure C.11-21. FID chromatogram obtained from the capillary GC analysis of the base/neutral priority pollutant standard shown analyzed in Figure C.11-17.

C.11-46

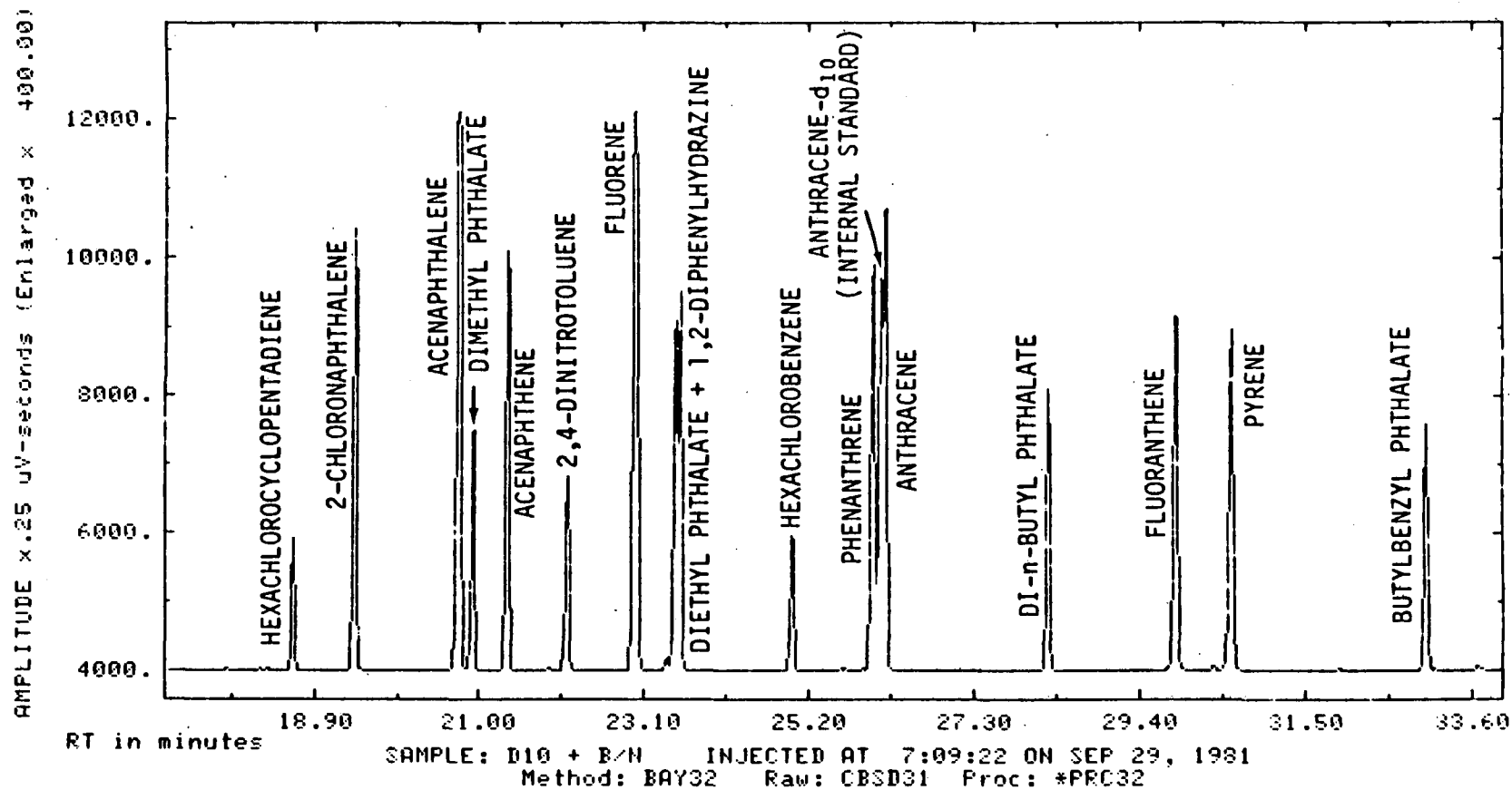


Figure C.11-21 (continued)

C.11-47

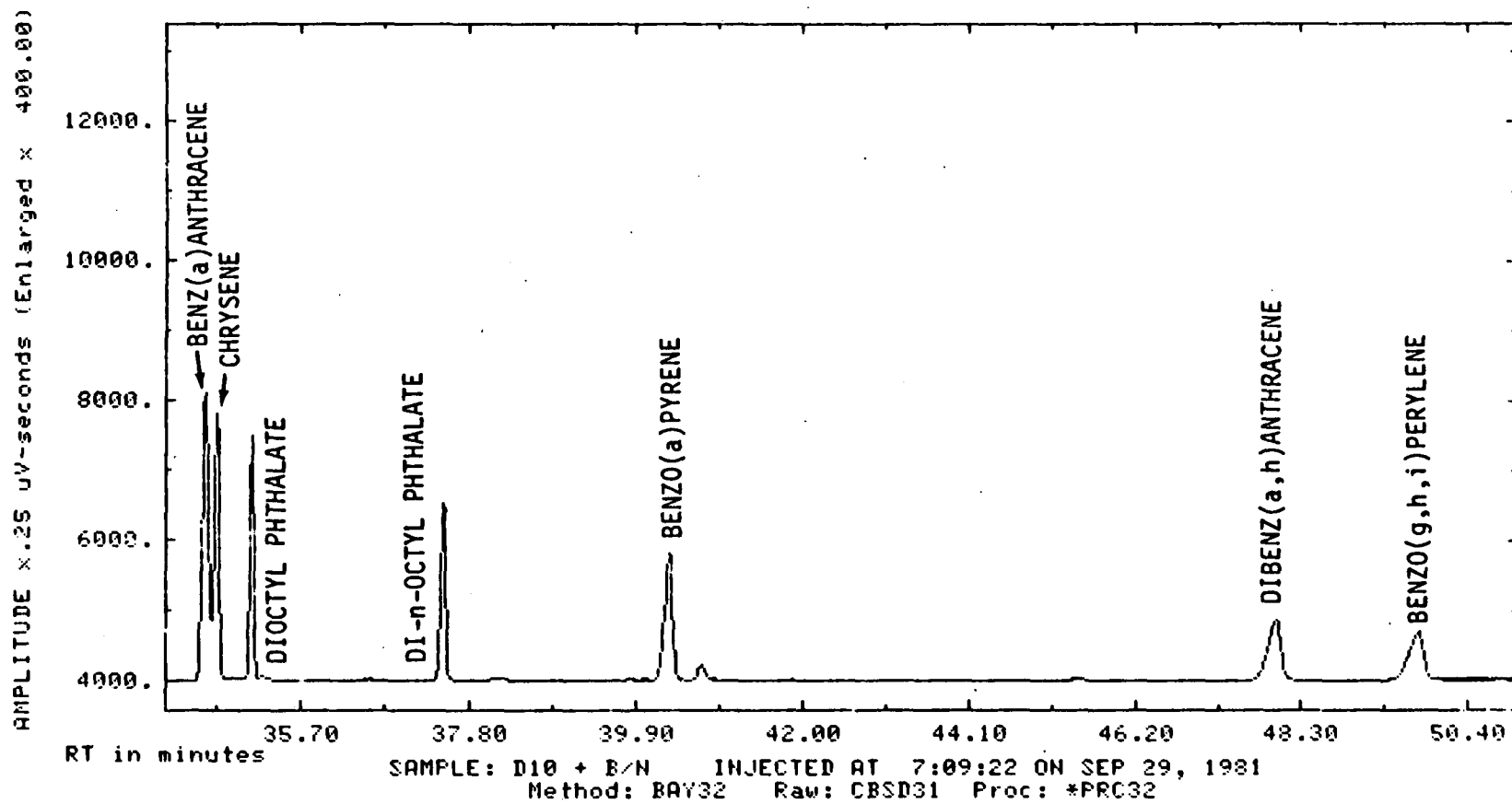


Figure C.11-21 (continued)

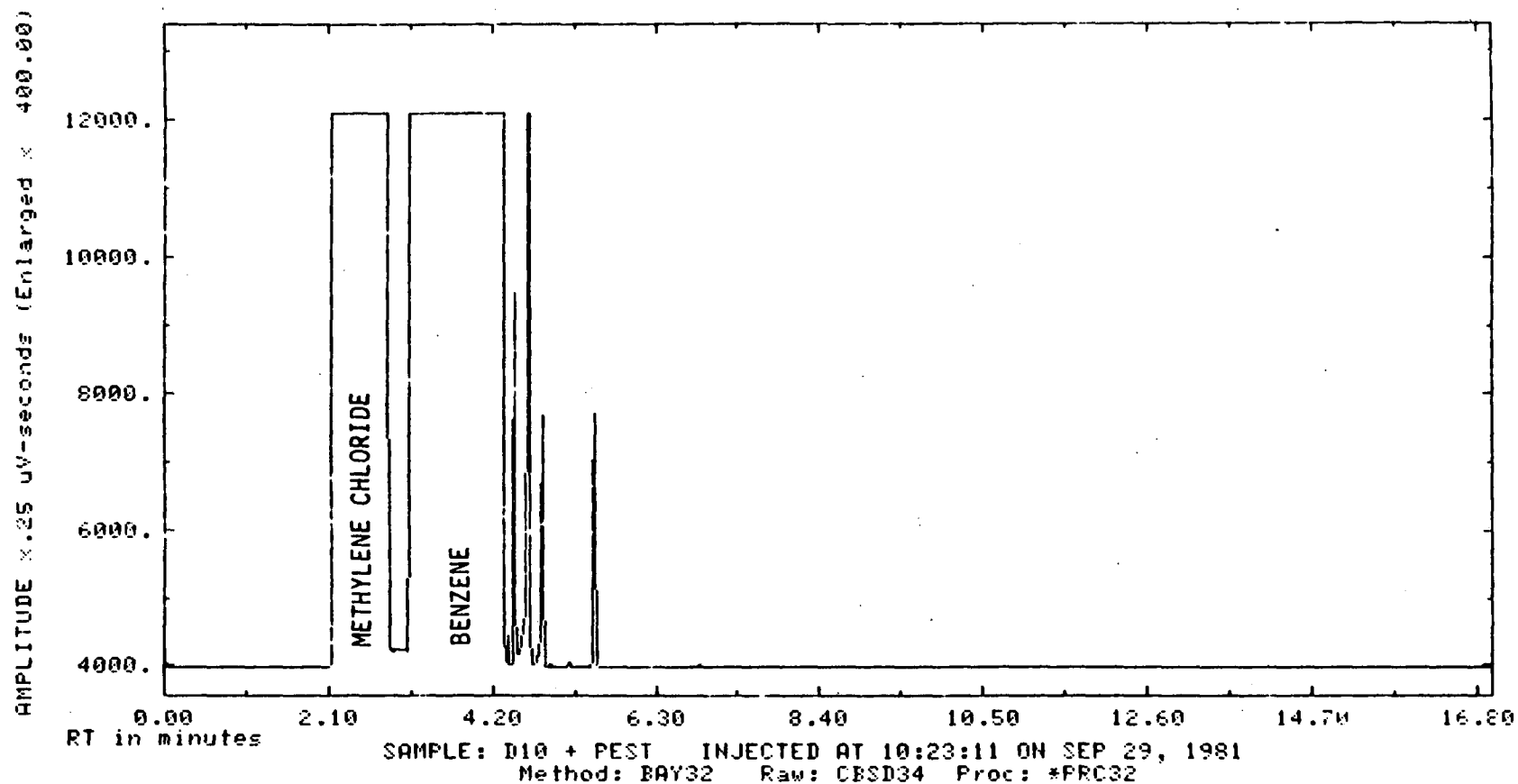


Figure C.11-22. FID chromatogram obtained from the capillary GC analysis of the pesticide priority pollutant standard shown analyzed in Figure C.11-18.

C.11-49

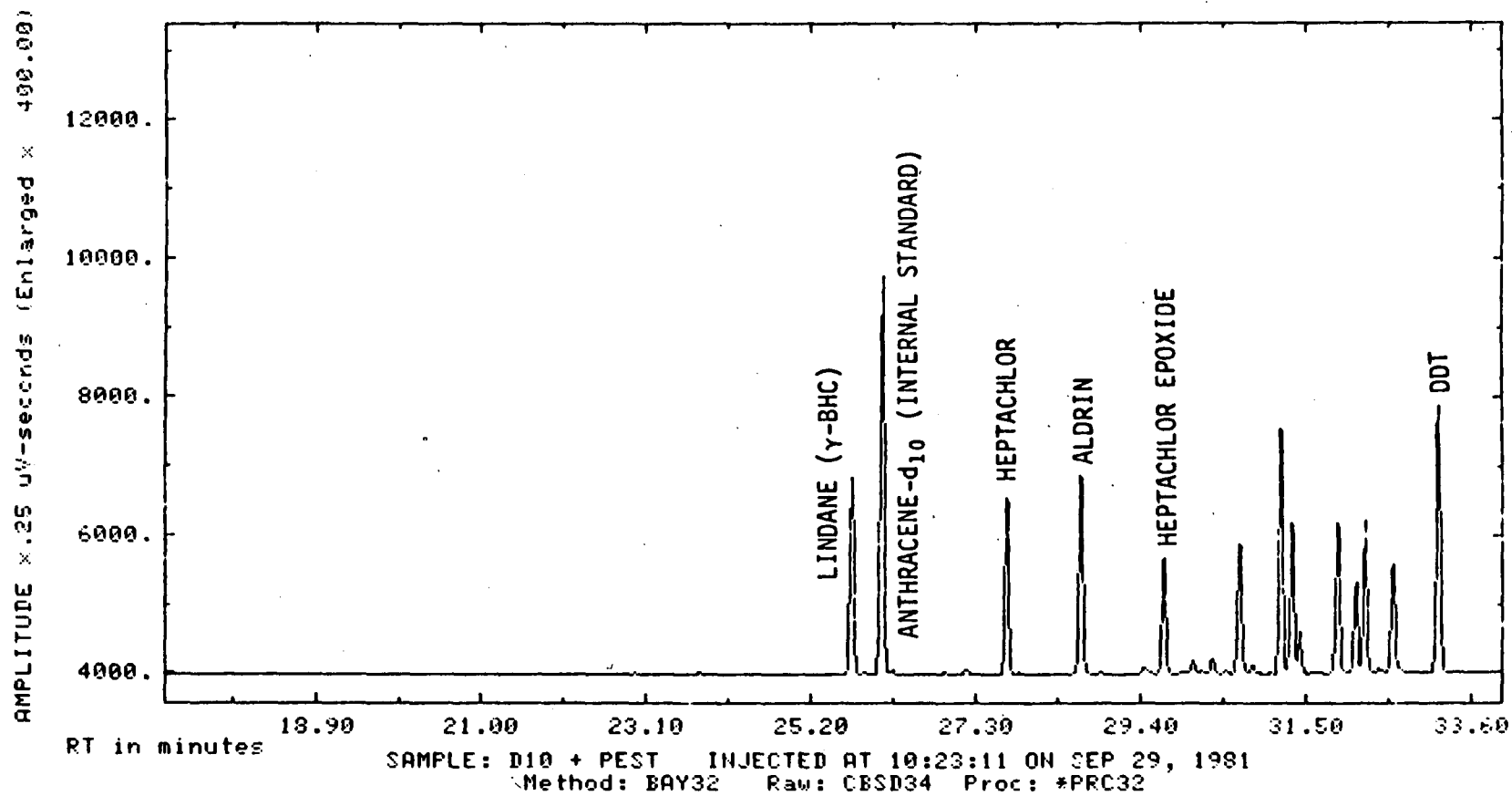


Figure C.11-22 (continued)

C.12 BIOACCUMULATION ANALYSIS OF EFFLUENTS

Effluent samples were tested to determine the bioaccumulation potential of organic constituents. Resulting data provide information on the potential for bioaccumulation of organic compounds in aquatic species. The data also were used to aid in the estimation of the severity of toxic effects of organic constituents; i.e., if compounds are found to be toxic by bioassay techniques and also bioaccumulate, the severity is compounded [16].

The test method used was the octanol/water partition coefficient high performance liquid chromatographic (HPLC) method described in the Federal Register [17]. Specific correlations exist between octanol/water partition coefficients (P) and bioconcentration in fish. A compound with a log P greater than or equal to 3.5 indicates a tendency of that compound to accumulate in lipoid tissues. Other recognized methods to obtain log P include direct measurement of the concentration of the chemical in an equilibrated octanol/water system.

The HPLC method has an advantage over the direct measurement of log P because it is a rapid, inexpensive method of identifying, without previous separation or identification, those mixtures which contain compounds that pose a potential bioaccumulative hazard.

Samples extracted in methylene chloride were analyzed for their bioaccumulative potential by HPLC under the following conditions: utilization of a Waters Radial Pak A column, a 15% H₂O/85%

[16] Bieri, R. H., M. K. Cueman, R. J. Huggett, W. MacIntyre, P. Shoa, C. W. Su, and G. Ho. Investigation of Organic Pollutants in the Chesapeake Bay; Report #1, Grant R806012010, submitted to the U.S. Environmental Protection Agency, Chesapeake Bay Program, Annapolis, Maryland.

[17] Federal Register, 43:243, 18 December 1978.

methanol mobile phase, a detector wavelength of 254 nm, and a flow rate of 1.0 mL/min. The samples containing organic constituents are eluted in order of hydrophilicity and increasing octanol/water partition coefficient.

C.12.1 Instrument Calibration

The instrument calibration was determined daily by injecting 10.0 μ L of a solution containing:

<u>Compound</u>	<u>Concentration, μg/mL</u>
Benzene	215
Bromobenzene	510
Biphenyl	10
Bibenzyl	510
p,p'-DDE	33
PCB	93

A linear regression equation of the form $\log P = X \log t_R + Y$ was determined from the retention times and literature $\log P$ values of the above compounds:

$$\text{where } P = \frac{\text{concentration in octanol}}{\text{concentration in water}}$$

when the chemical is in equilibrium between octanol and water and t_R (retention time) is the time from sample injection to maximum concentration (peak height) of eluted compound. The geometric mean of the instrument response, expressed as μ g/25% full-scale deflection (FSD) was calculated in order to determine instrument sensitivity (IS). The results of these calculations are shown on the following page. Figure C.12-1 gives the plot of $\log P$ vs. $\log t_R$.

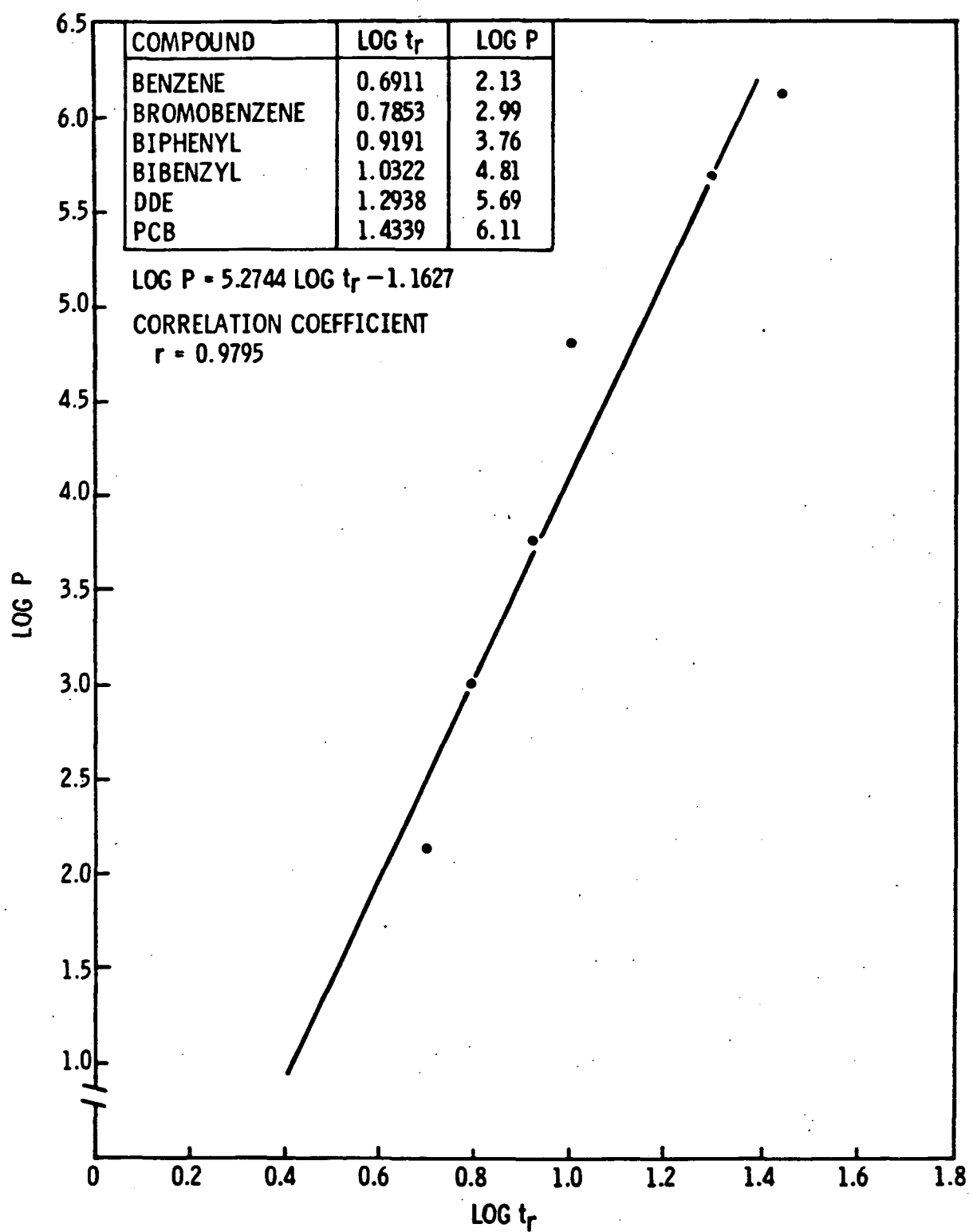


Figure C.12-1. Graph of log P vs. log t_R .

Compound	Log P [2]	t _R	Log t _R ^b	μg injected	cm peak height	% FSD ^b	μg/25% FSD ^c
Benzene	2.13	4.91	0.6911	2.15	5.5	36.7	1.46
Bromobenzene	2.99	6.10	0.7853	5.10	5.1	34.0	3.75
Biphenyl	3.76	8.30	0.9191	0.10	7.7	51.3	0.05
Bibenzyl	4.81	10.77	1.0322	5.10	6.4	42.7	2.99
p,p'-DDE	5.69	19.67	1.2938	0.33	5.4	36.0	0.23
PCB	6.11	27.16	1.4339	0.93	2.0	13.3	1.75

Geometric mean^d = IS = 0.831 μg/25% FSD

^aThe linear regression equation was determined with a Texas Instrument TI-55 calculator from the literature values of log P and the determined values of log t_R.

$$\text{Log P} = 5.2744 \text{ Log } t_R - 1.1627$$

Correlation coefficient, r = 0.9795

^b% FSD = Percent full-scale deflection, FSD = 15 cm on the recorder used for these determinations.

$$\% \text{ FSD} = \frac{\text{cm peak height}}{\text{FSD (in cm)}} \times 100$$

^cμg/25% FSD determined by:

$$\mu\text{g}/25\% \text{ FSD} = \mu\text{g injected} \times \frac{25}{\% \text{ FSD}}$$

$$\text{Geometric mean} = \sqrt[6]{(1.46)(3.75)(0.05)(2.99)(0.23)(1.75)} = 0.831$$

The instrument sensitivity (IS) in μg equals X, the number of liters of water to be extracted for a mean sensitivity of 1 ppb.

C.12.2 Example of a Typical Analysis

One liter of water sample was extracted with three, 50-mL portions of methylene chloride. The extract was dried by passing through a column of sodium sulfite and the volume was reduced to 1.0 mL. A ten-microliter (10-μL) portion of this extract was analyzed by HPLC. The chromatogram in Figure C.12-2 shows that 23 peaks eluted within 44.08 minutes. The results and calculations from this analysis are tabulated on page C.12-6.

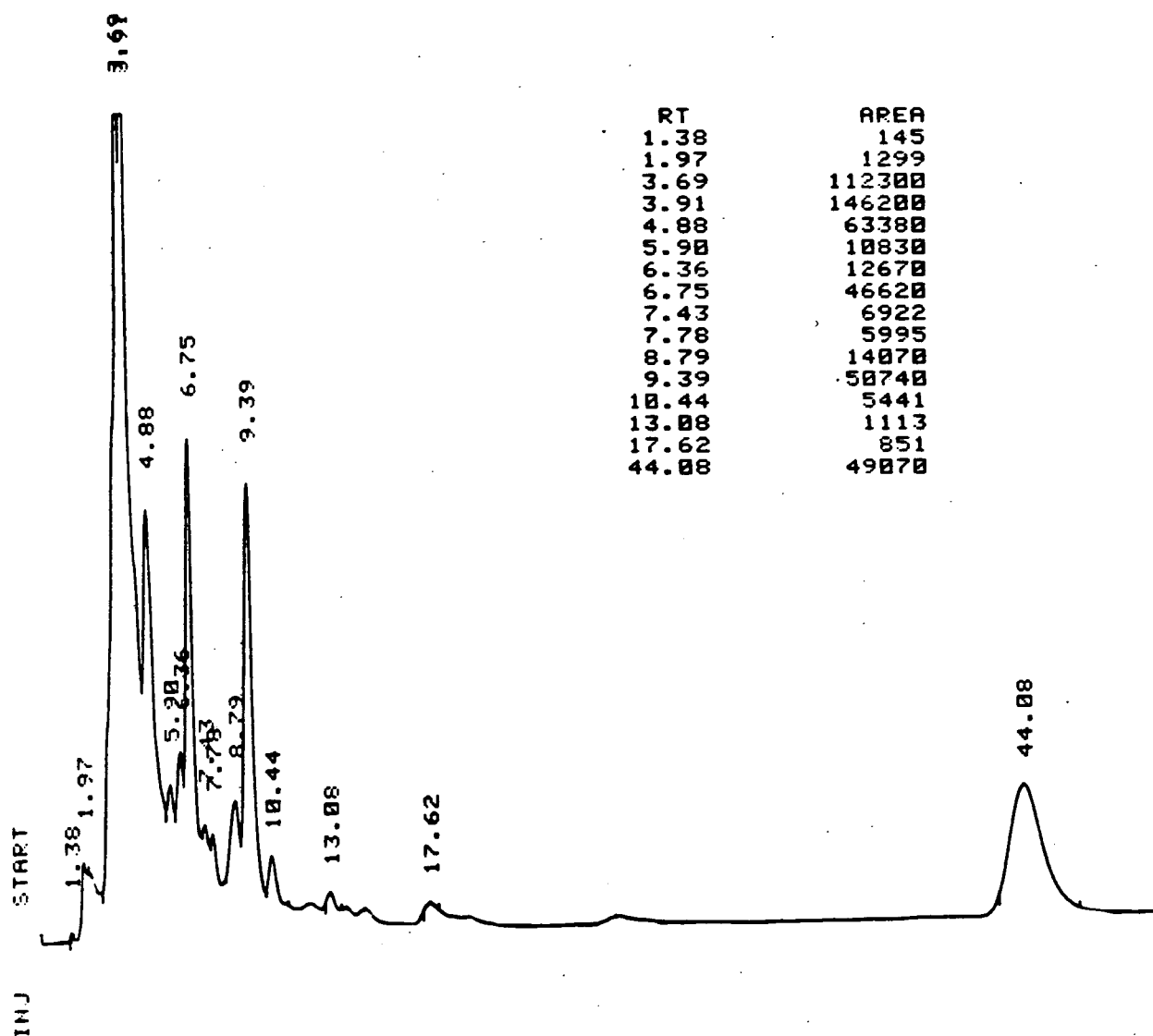


Figure C.12-2. HPLC chromatogram for a typical bioaccumulation potential analysis.

Peak No.	t _R	Log t _R	Calcd. log P	Peak height, cm	Adj. ^a peak height, cm	FSD ^b , %	Est. conc ^c , index ^c , ppb	Potential for bioaccumulation ^d positive/negative
1	1.38	0.1399	-0.35	0.15	14	91	4	-
2	1.97	0.2945	0.39	1.4	130	850	34	-
3	2.38	0.3766	0.78	1.2	110	730	29	-
4	3.69	0.5670	1.69	>15	>1,400	>9,100	>360	-
5	3.91	0.5922	1.81	>15	>1,400	>9,100	>360	-
6	4.88	0.6884	2.26	7.8	710	4,700	190	-
7	5.90	0.7709	2.66	2.8	260	1,700	68	-
8	6.36	0.8035	2.81	3.4	310	2,100	83	-
9	6.75	0.8293	2.93	9.1	830	5,500	220	-
10	7.4	0.8710	3.13	2.0	180	1,200	49	-
11	7.76	0.8899	3.22	1.9	170	1,200	46	-
12	8.79	0.9440	3.48	2.4	220	1,500	58	-
13	9.39	0.9727	3.62	8.3	760	5,000	200	+
14	10.44	1.0187	3.83	1.4	130	850	34	+
15	11.25	1.0512	3.99	0.5	46	300	12	+
16	12.25	1.0881	4.16	0.5	46	300	12	+
17	13.08	1.1166	4.30	0.7	64	430	17	+
18	13.88	1.1424	4.42	0.4	36	240	10	+
19	14.75	1.1688	4.55	0.4	36	240	10	+
20	17.62	1.2460	4.92	0.4	36	240	10	+
21	19.50	1.2900	5.13	0.2	18	120	5	+
22	26.00	1.4150	5.72	0.15	14	91	4	+
23	44.08	1.6442	6.81	2.4	220	1,500	58	+

$$^a \text{Adjusted Peak Height} = \frac{V_E \times H}{V_I}$$

where V_E = volume (μL) of methylene chloride extract after volume reduction
V_I = volume (μL) injected (normally 10 μL)
H = peak height (cm)

If the volume of water extracted does not equal X, the adjusted peak height can be determined by:

$$\text{Adjusted Peak Height} = \frac{V_E}{V_I} \times \frac{X}{V_W} \times H$$

where V_E = volume (μL) of methylene chloride extract after volume reduction
V_I = volume (μL) injected (normally 10 μL)
H = peak height (cm)
X = experimentally determined from instrument sensitivity (L)
V_W = volume of water extracted (L)

$$^b \% \text{ FSD} = \frac{\text{adjusted cm peak height}}{\text{FSD (in cm)}} \times 100$$

$$^c \text{Estimated concentration, ppb} = \frac{\% \text{ FSD}}{25}$$

This calculation is based on the experimentally determined instrument sensitivity and may be in error by 2 orders of magnitude or more due to the varying UV response of different compounds at 254 nm.

^d A positive response is defined as an instrumental response greater than or equal to 25% full-scale deflection in the region of log P greater than or equal to 3.5.

Figure C.12-2 (continued)

C.12.3 Sample Calculation for Peak 23 (44.08 min) of a Typical Sample

C.12.3.1 Instrumental Response--

$$\text{Adjusted Peak height} = \frac{V_E}{V_I} \times \frac{X}{V_W} \times H$$

$$V_E = 1,000 \mu\text{L}$$

$$V_I = 10 \mu\text{L}$$

$$H = 2.4 \text{ cm}$$

$$X = 0.911 \text{ L}$$

$$V_W = 1.0 \text{ L}$$

$$\text{Adjusted Peak height} = \frac{1,000 \mu\text{L}}{10 \mu\text{L}} \times \frac{0.911 \text{ L}}{1.0 \text{ L}} \times 2.4 \text{ cm}$$

$$\text{Adjusted peak height} = 220 \text{ cm}$$

$$\% \text{ Full-scale deflection} = \frac{\text{adjusted cm peak height}}{\text{FSD (in cm)}} \times 100$$

$$= \frac{220 \text{ cm}}{15 \text{ cm}} \times 100$$

$$\% \text{ Full-scale deflection} = 1,500$$

Note that this calculation results in %FSD >100%.

C.12.3.2 Determination of Log P--

$$t_R = 44.08; \text{Log } t_R = 1.6442$$

Using the linear regression equation $\text{Log } P = 4.7565 \text{ Log } t_R - 1.0109$, the value for log P is 6.81.

Therefore, Peak 23 gives a positive response since the instrumental response is greater than or equal to 25% of the full-scale deflection and the value of log P is greater than or equal to 3.5.

C.12.4 Data Correlation

An attempt was made to determine the chemical identity of the positive bioaccumulation responses found in the samples. The chemical structure of the presurvey compounds and GC/MS identified compounds listed with their literature value log P [18-26].

-
- [18] Gould, R. F., editor. Biological Correlations - The Hansch Approach. Adv. Chem. Ser. #114. American Chemical Society, Washington, D.C., 1972.
 - [19] Veith, G. D., and D. E. Konasewich. Structure-Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms. International Joint Commission Publication, Windsor, Ontario, 1975. 347 pp.
 - [20] Carlson, R. M., H. L. Kopperman, and R. E. Carlson. Structure Activity Relationships Applied.
 - [21] Neeley, W. G., D. R. Branson, and G. E. Blau. The Use of the Partition Coefficient to Measure the Bioaccumulation Potential of Organic Chemicals in Fish. Environ. Sci. Technol. 8:1113-1115, 1974.
 - [22] Chiou, C. T., V. H. Freed, D. W. Schmedding, and R. L. Kohnert. Partition Coefficient and Bioaccumulation of Selected Organic Chemicals. Environ. Science and Technol. 11(5):475-478, 1977.
 - [23] Vieth, G. D., and N. Austin. Detection and Isolation of Bioaccumulable Chemicals in Complex Effluents. In: Identification and Analysis of Organic Pollutants in Water, L. H. Keith ed. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1976. pp. 297-302.
 - [24] Hansch, C., and T. Fujita. A Method for the Correlation of Biological Activity and Chemical Structure. J. Am. Chem. Soc., 86:1616-1626, 1964.
 - [25] Leo, A., C. Hansch, and D. Elkins. Partition Coefficients and Their Uses. Chem. Rev., 71:525-616, 1976.
 - [26] Hansch, C. Computerized Printout of Log P Values by Increasing Log P and Increasing Molecular Carbon Content. Pomona College, Claremont, California.

The actual log P values found in the samples were then compared with this information, and any potential correlations were noted. Experiments conducted at MRC indicated that the HPLC technique for log P and the published literature values agreed ± 0.05 for polar compounds which are typically more bioaccumulative than nonpolar ones. This number was used as the criteria for determining any correlations.

In addition, log P values found in the samples which had no potential presurvey or GC/MS compound correlation were compared to the log P literature to attempt to tentatively identify the species, using the ± 0.05 criteria while looking in the literature for compounds of a similar nature to those identified by GC/MS (e.g., compounds that could be a wastewater treatment or extraction artifact of a previously identified compound).

C.12.5 QC/QA For Bioaccumulation Analysis

The following QC/QA procedures were practiced when performing Phase III bioaccumulation potential analyses:

- (1) The instrument sensitivity ($\mu\text{g}/25\%$ full-scale deflection) was determined daily by duplicate injection of a standard solution containing 215 $\mu\text{g}/\text{mL}$ benzene, 510 $\mu\text{g}/\text{mL}$ bromobenzene, 10 $\mu\text{g}/\text{mL}$ biphenyl, 510 $\mu\text{g}/\text{mL}$ bibenzyl, 33 $\mu\text{g}/\text{mL}$ p,p'-DDE, and 93 $\mu\text{g}/\text{mL}$ PCB.
- (2) The linear regression equation was determined daily from the values obtained from the log of the retention times and the Federal Register log P values for the calibration standards.
- (3) A minimum of 10% deionized water blanks were run with each set of analyses.

- (4) A minimum of 10% deionized water spikes (Federal Register calibration standards) were run with each set of analyses.
- (5) A minimum of 10% duplicate analyses were run with each set of analyses.

C.13 BIOACCUMULATION FRACTIONATION

In order to identify the potentially bioaccumulative compounds present in the effluent samples, the methylene chloride extracts were separated and fractionated by high performance liquid chromatography (HPLC). Each fraction was extracted and the extracts were analyzed by GC/MS.

C.13.1 Method Development

A mixture of six compounds used to calibrate the HPLC response used in the bioaccumulation studies, was used to develop an extraction method for the identification of major components in HPLC-fractionated samples. The standard solution contained benzene at 215 ppm, bromobenzene at 510 ppm, biphenyl at 10 ppm, bibenzyl at 510 ppm, p,p'-DDE at 33 ppm, and 2,2',4,5,5'-penta-chlorobiphenyl (PCB) at 93 ppm in hexane. One hundred microliters of this standard solution was added to 25 mL of a methanol/water (85/15) solvent system identical to that used for HPLC separation and fractionation. The spiked methanol/water solution was concentrated to approximately 8 mL using a Kuderna-Danish apparatus. Three, 3.5-mL portions of methylene chloride were used to extract the concentrated methanol/water solution. After extraction, the methylene chloride extract was dried and concentrated using either a stream of dry nitrogen or a Kuderna-Danish evaporator. Table C.13-1 summarizes recoveries measured using these two concentration steps. Generally better recoveries were observed using Kuderna-Danish evaporation which was therefore used for the concentration of the methylene chloride extracts of fractions from Plants B112D, B149S, B141S, C161D, C150D, and B119D.

C.13.2 HPLC Fractionation

The methylene chloride extracts from selected plant effluents were separated by HPLC and automatically fractionated using a

TABLE C.13-1. EXTRACTION RECOVERIES

Compound	Percent recovery	
	Nitrogen evaporation	Kuderna-Danish evaporator
Bromobenzene	0	0
Biphenyl	59.2	81.9
Bibenzyl	80.0	113
p,p'-DDE	66.9	87.7
2,2',4,5,5'-PCB	71.7	97.8

Hewlett-Packard 1084B liquid chromatograph and a fraction collection accessory. Ten, 10- μ L injections were made, and two to five fractions per extract were collected. The decision as to which fractions to separate was effected by the amount of the compound present and the calculated Log P values. The HPLC fractions were extracted according to the procedure described in C.13.1 and analyzed by GC/MS.

C.13.3 Results

The extracts of the HPLC fractions were analyzed by capillary GC/MS. The method blank, instrument blank, and fraction extracts contained large amounts of well resolved peaks which did not interfere with the determination of the major components of the plant fractions.

C.13.3.1 Plant B149S--

Figure C.13-1 shows the HPLC chromatogram of the methylene chloride extract of Plant B149S effluent with the four fractions indicated. The approximate Log P range of the components in the fractions were:

<u>Fraction</u>	<u>Approximate log P range</u>
1	3.6 to 3.8
2	4.2 to 4.5
3	4.9 to 5.0
4	5.7 to 5.8

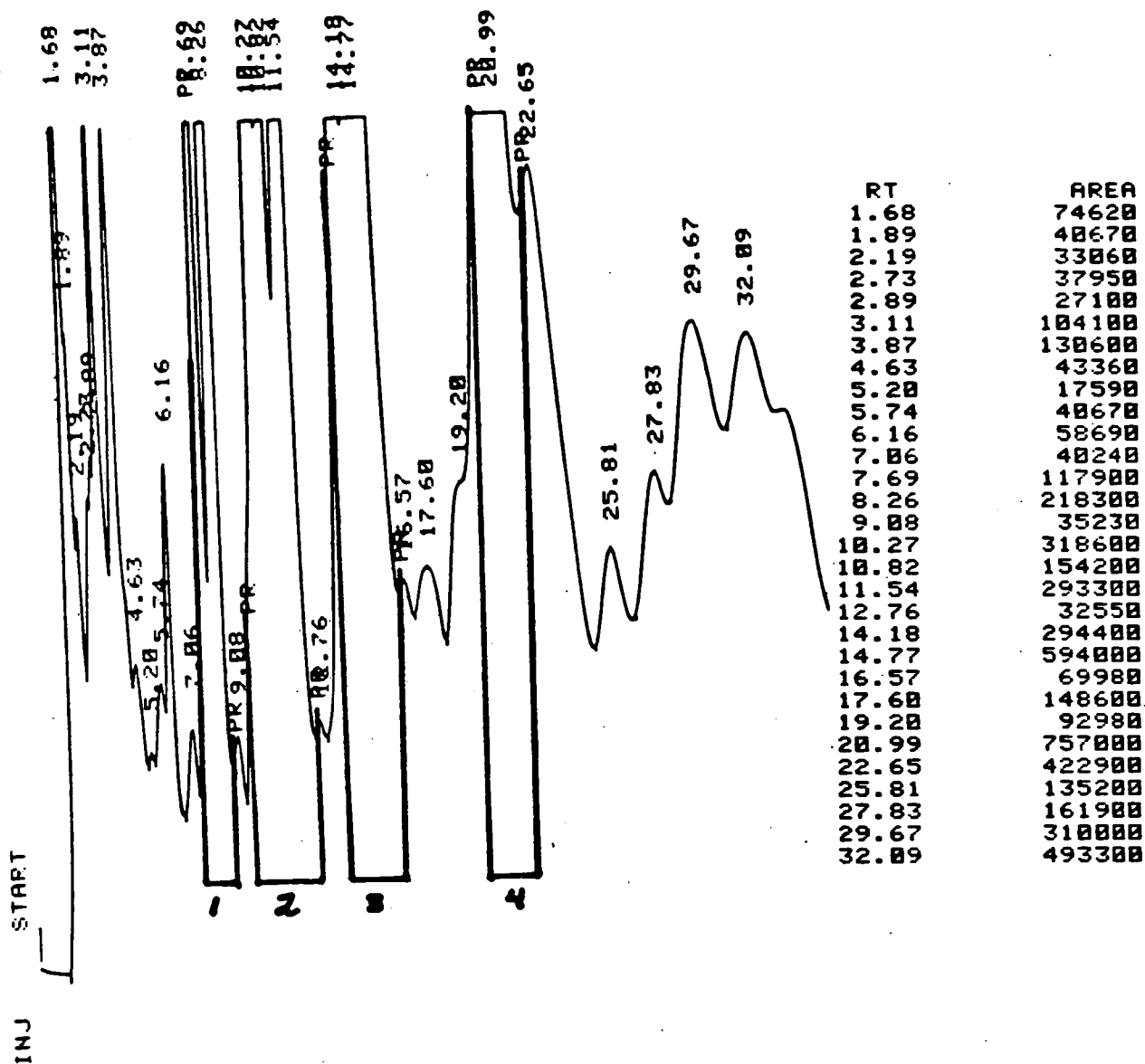


Figure C.13-1. HPLC chromatogram of extract of effluent B149S.

Figure C.13-2 compares the total ion chromatograms obtained from the analysis of the method blank and four fraction extracts of Plant B149S. The major components of fraction 1 are 1- and 2-methyl naphthalene which elute between 13 and 14 minutes. The small component eluting at approximately 14.8 minutes is biphenyl. The literature Log P value of biphenyl is 3.76 which agrees with the 3.6 to 3.8 Log P range of fraction 1. The major components of fraction 2 which elute in the 15 to 16 minute range, are dimethyl naphthalene isomers. The group of peaks which elute between 9 and 11 minutes are tetramethyl benzene isomers.

Fraction 3 of the Plant B149S extract contains a large number of low-level components. The compounds which elute between 17 and 18 minutes are trimethyl naphthalene isomers. Those which elute between 10 and 14 minutes have not been completely identified. However, dimethyl tetrahydronaphthalene appears to be present.

Fraction 4 of the Plant B149S extract also contains a large number of components. The major component which elutes at 11.4 minutes is n-dodecane (C_{12} normal hydrocarbon). The other compounds which elute between 12 and 15 minutes also appear to be hydrocarbons, however the levels are too low to attempt identification.

We were not requested to analyze completely the acid and base/neutral fractions from Plant B149S. However, capillary GC/MS data were acquired for these extracts, due to the very high TCO values obtained. Figure C.13-3 shows the molecular ion chromatograms for methyl naphthalene and dimethyl naphthalene isomers obtained from the analysis of capillary GC/MS data of the diluted base/neutral extract from Plant B149S. As can be seen, large amounts of these two compounds are present in the base/neutral extract. Note that the relative intensities of the m/e 142 mass chromatogram are very similar to the total ion chromatogram obtained from analysis of fraction 1 and that the relative intensities of the peaks in the m/e 156 mass chromatogram are very

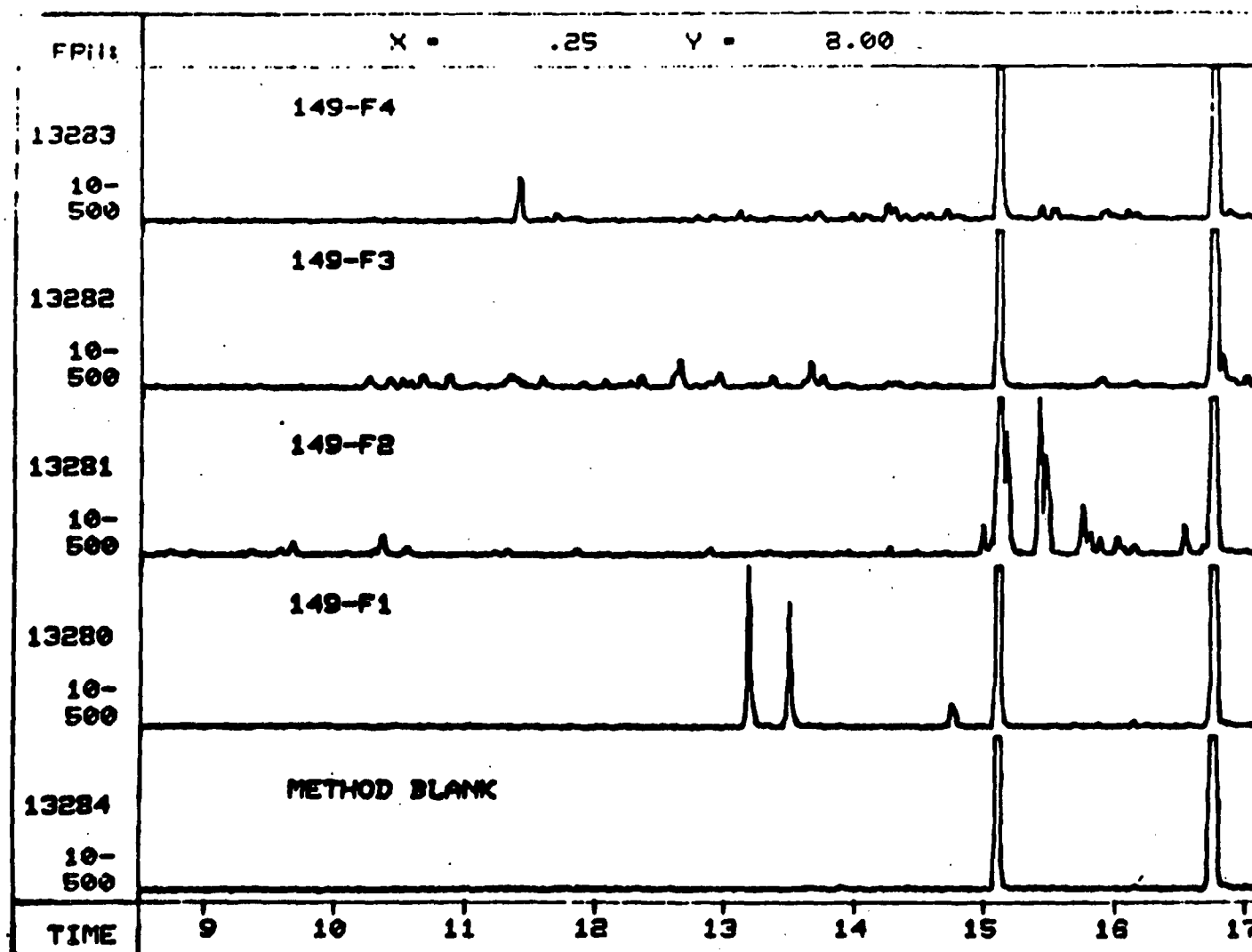


Figure C.13-2. Total ion chromatograms obtained from capillary GC/MS analysis of the method blank and four HPLC fractions of a methylene chloride extract of effluent B149S (no significant response occurred after 25 min).

C.13-6

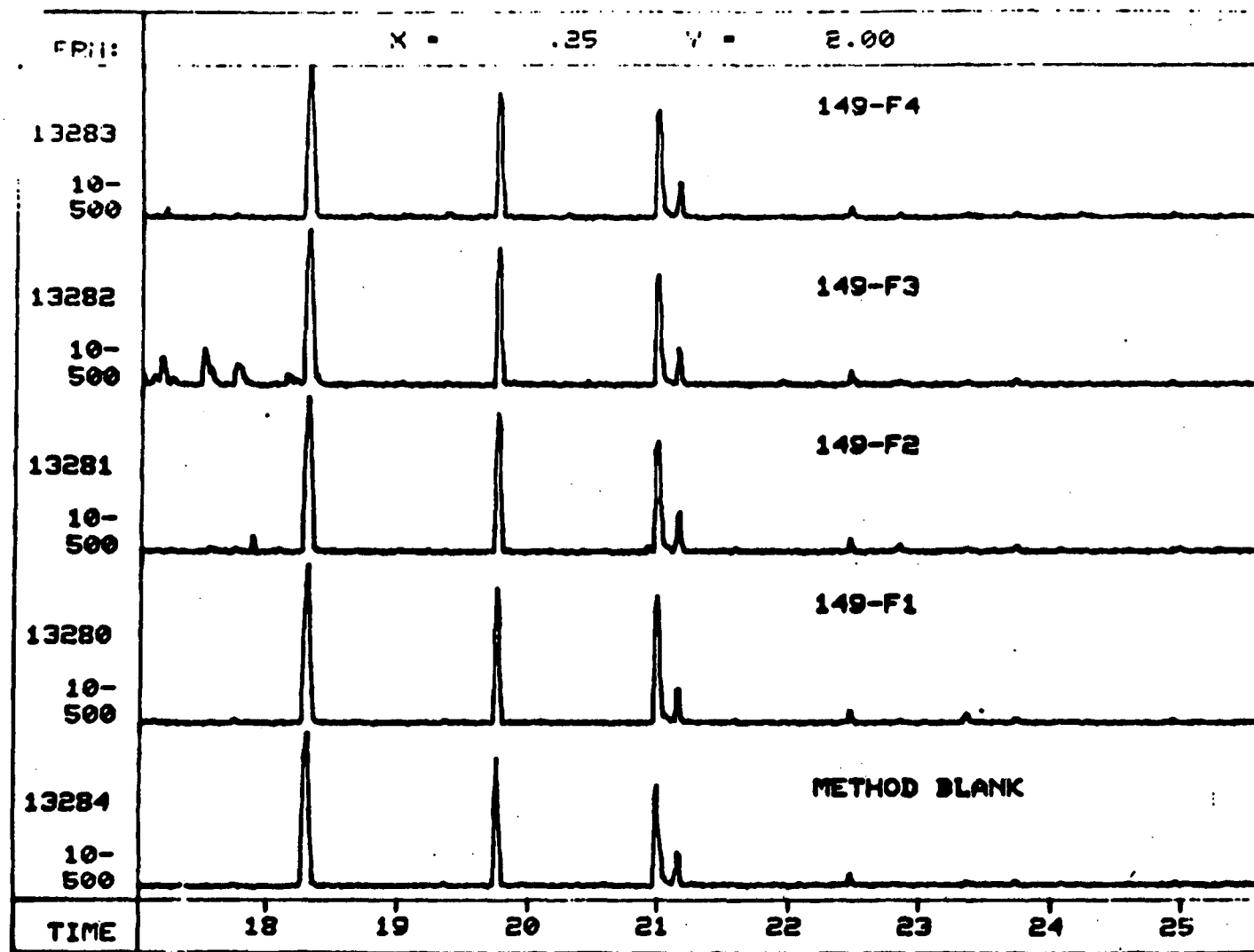


Figure C.13-2 (continued)

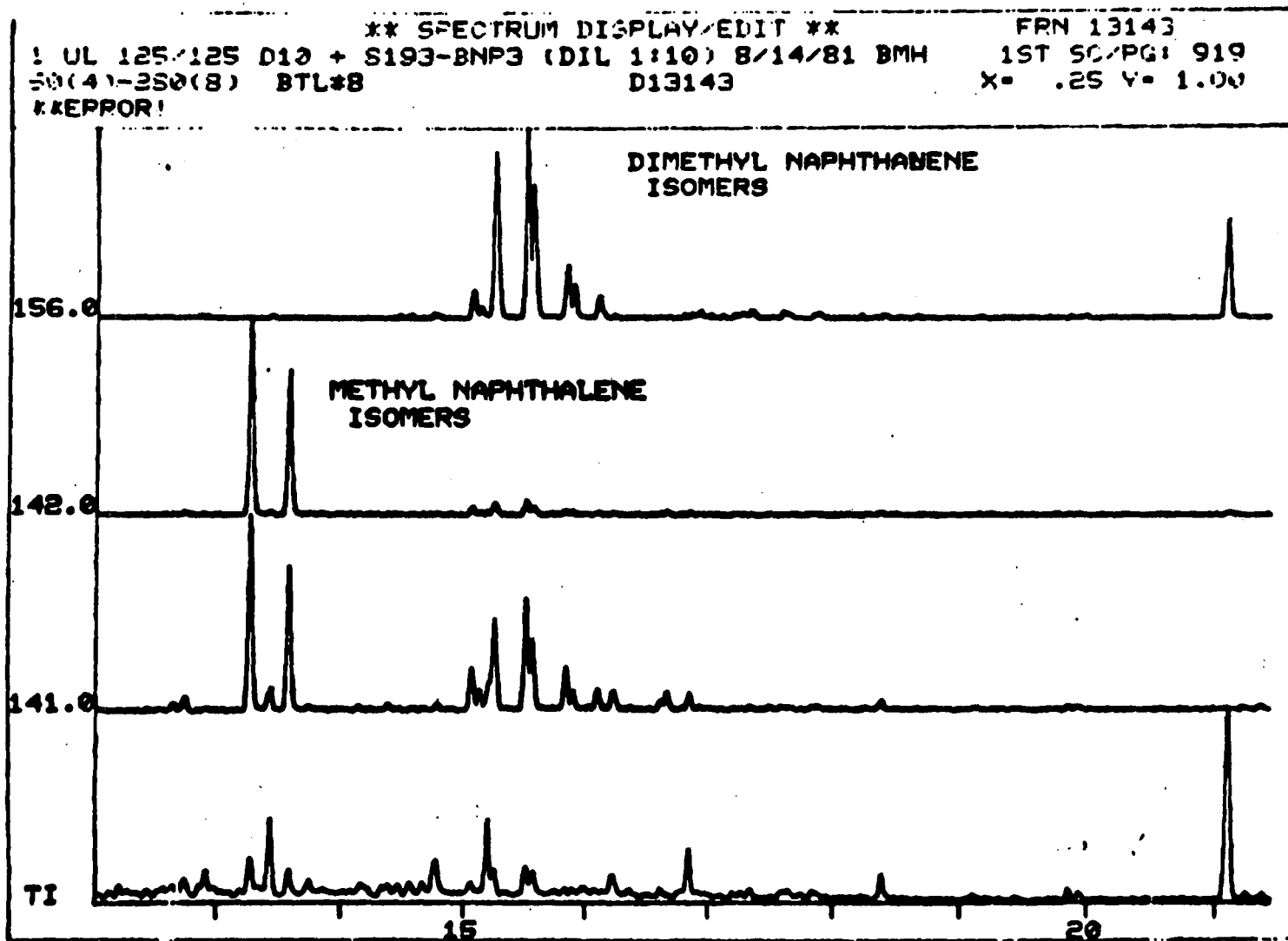


Figure C.13-3. Molecular ion chromatograms of methyl and dimethyl naphthalene isomers present in the base/neutral extract of effluent B149S.

similar to the major components in fraction 2 (exclusive of the large impurity peaks).

C.13.3.2 Plant B112D--

Figure C.13-4 shows the HPLC chromatogram of the methylene chloride extract of Plant B112D effluent with the four fractions indicated. The approximate Log P ranges of the components in the fractions were:

<u>Fraction</u>	<u>Approximate log P range</u>
1	4.1 to 4.5
2	4.9 to 5.1
3	5.3 to 5.6
4	5.8 to 5.9

Figure C.13-5 compares the total ion chromatograms obtained from the analysis of the method blank and four fraction extracts of Plant B112D. Only the first fraction of the Plant B112D effluent contained significant amounts of chromatographable compounds in excess of those found in the method blank. The compounds eluting between 15 and 16 minutes are dimethyl naphthalene isomers. The prominent peak at 16.5 minutes is acenaphthene. The peak at 18.1 minutes is fluorene and the peak at 20.9 minutes is phenanthrene. Experimentally determined Log P values for acenaphthene, fluorene, and phenanthrene are 4.15, 4.11, and 4.30, respectively. These values agree with the approximate Log P range of 4.1 to 4.5 for fraction 1. The concentration of acenaphthene in the original water sample, based upon the analysis of fraction 1, is approximately 450 µg/L. This is in good agreement with a value of 302 µg/L measured for this compound in the base/neutral extract of this plant's effluent and further demonstrates the feasibility of this approach in the identification of high levels of possible bioaccumulating compounds.

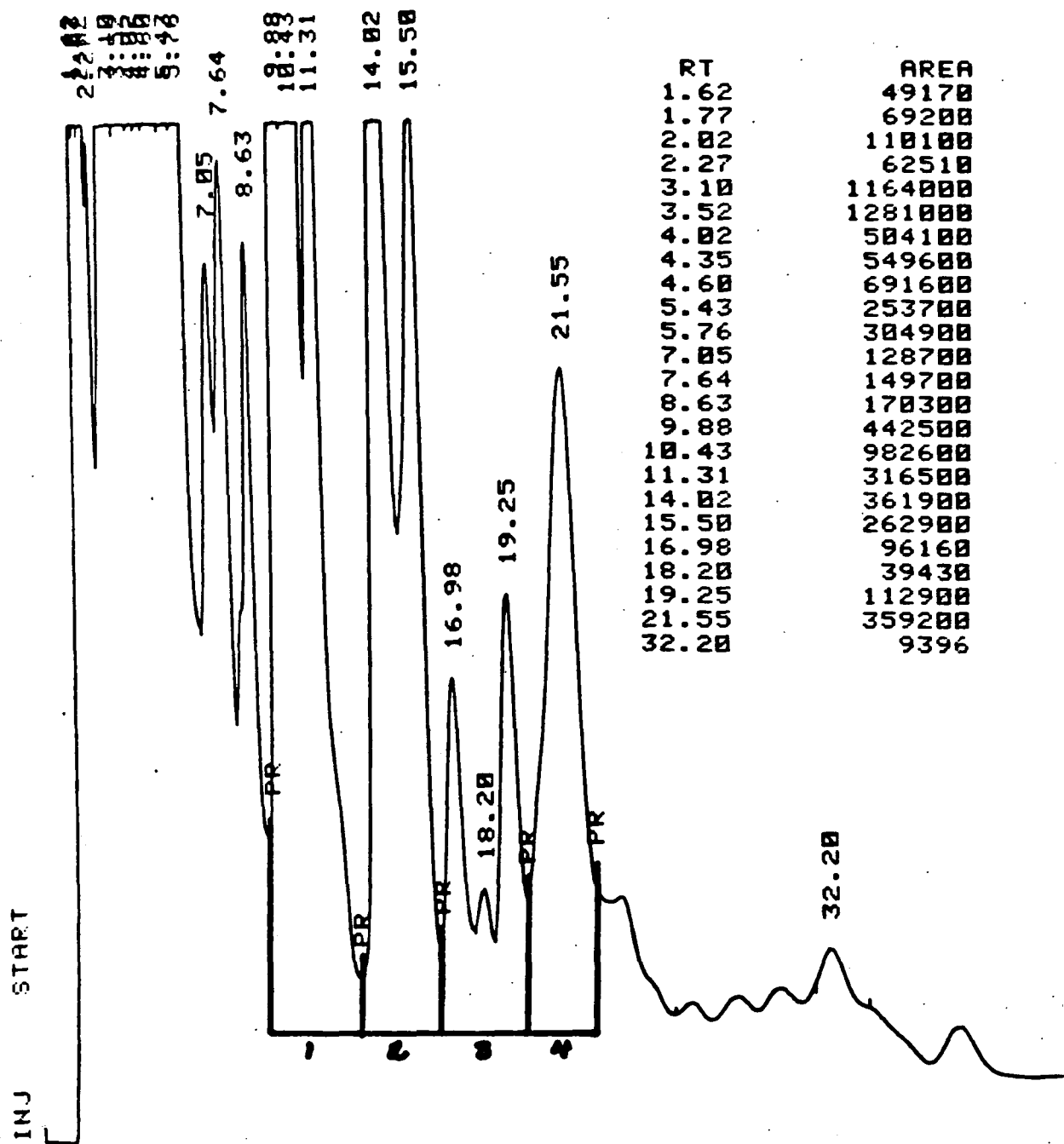


Figure C.13-4. HPLC chromatograms of extract of effluent B112D.

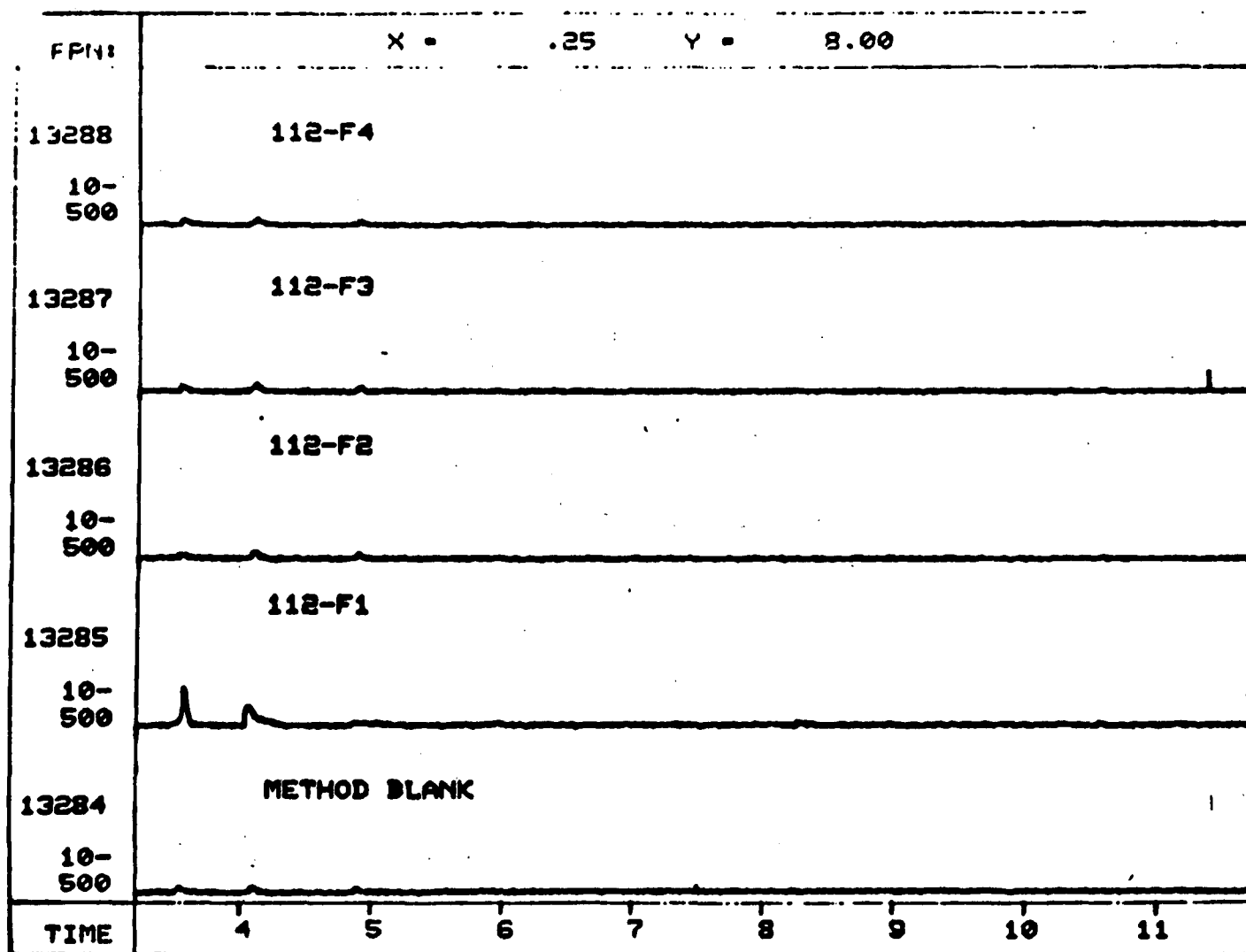


Figure C.13-5. Total ion chromatograms obtained from capillary GC/MS analysis of the method blank and four HPLC fractions of a methylene chloride extract of effluent B112D.

C.13-11

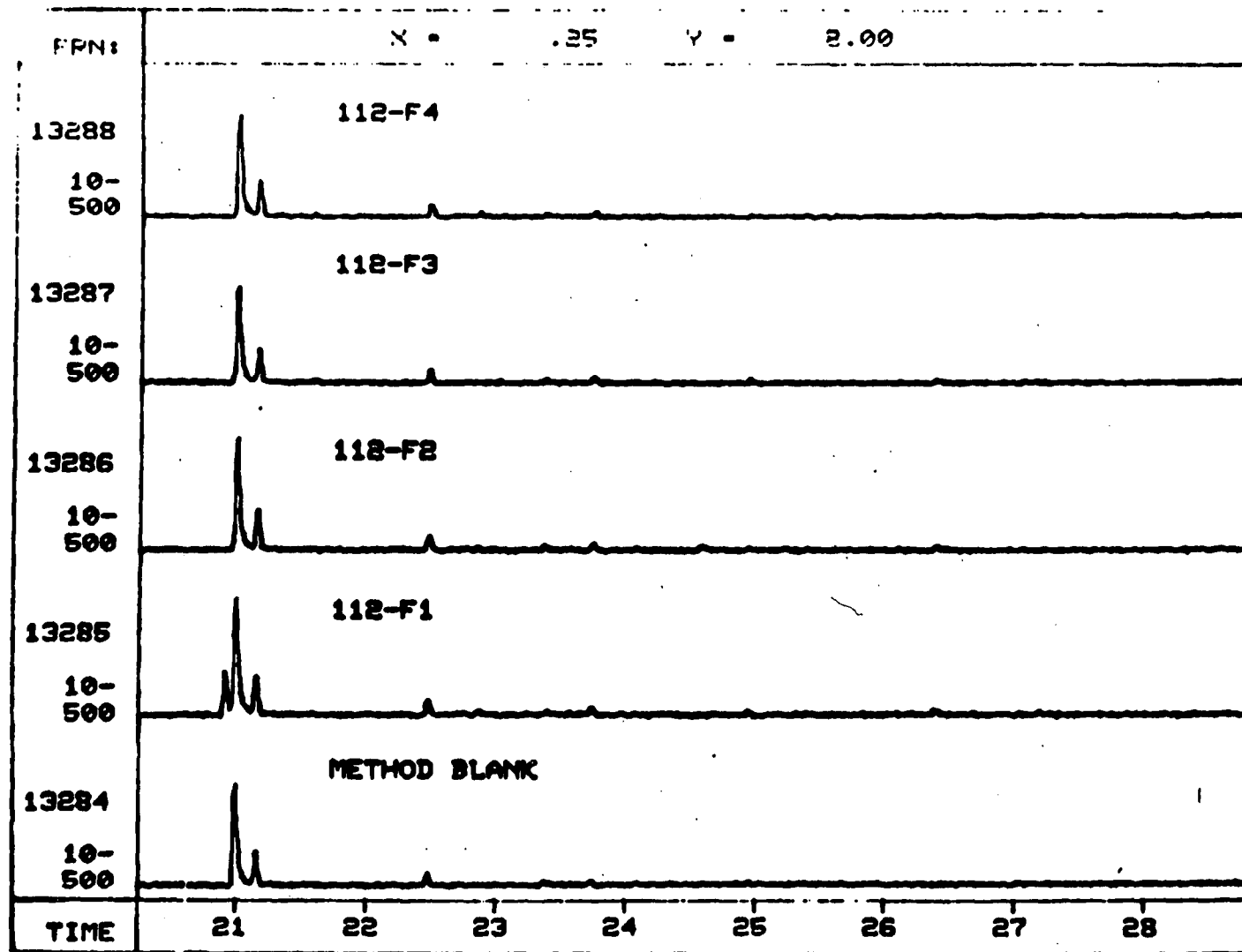


Figure C.13-5 (continued)

C.13-12

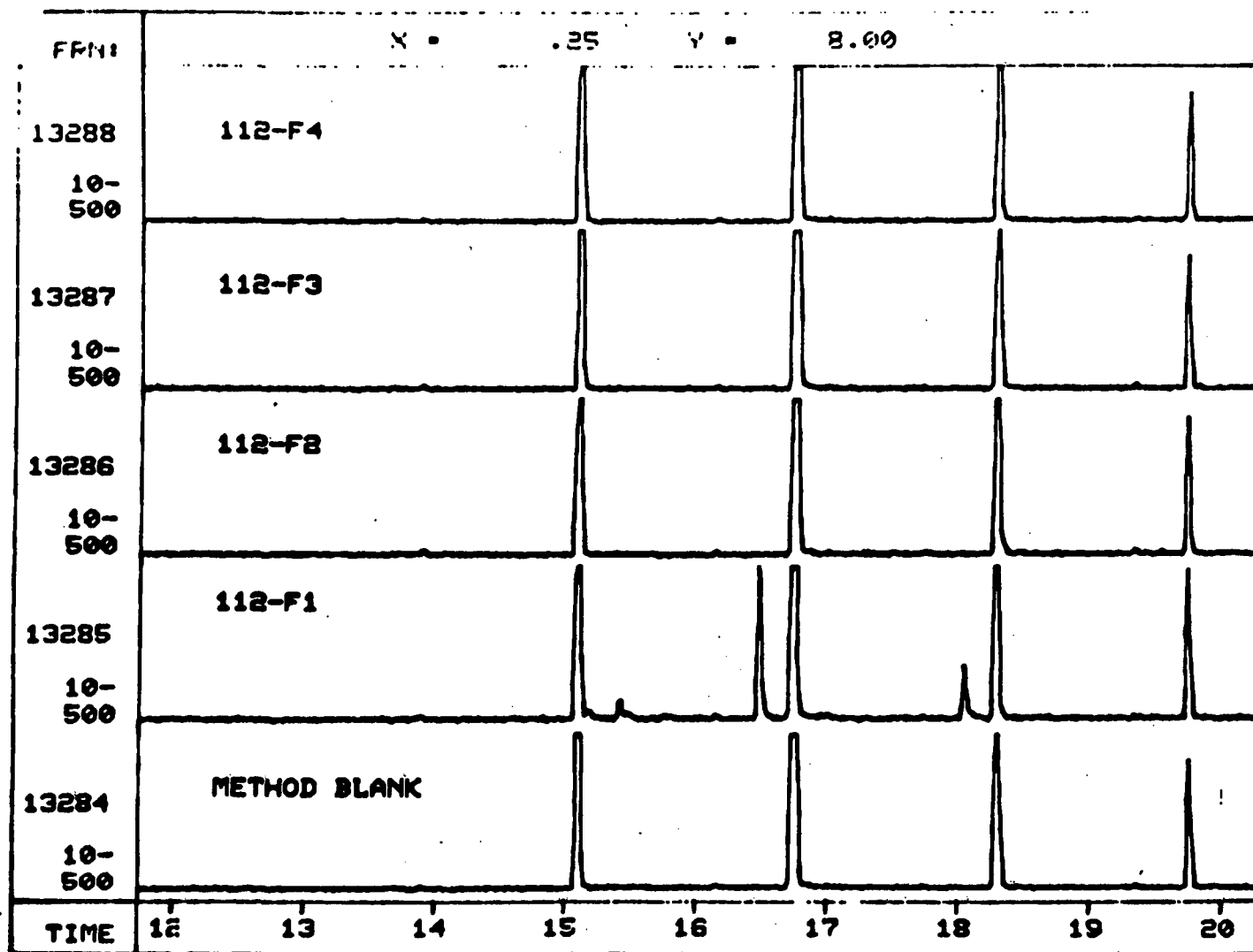


Figure C.13-5 (continued)

C.13.3.3 Plant B119D--

Figure C.13-6 shows the HPLC chromatogram of the methylene chloride extract of Plant B119D effluent with the two fractions indicated. The approximate Log P range of the components in the fractions were:

<u>Fraction</u>	<u>Approximate log P range</u>
1	3.5 to 3.6
2	3.9 to 4.0

Figure C.13-7 compares the total ion chromatograms obtained from two fractions from the extract of Plant B119D effluent with an HPLC method blank. The blank gave compound peaks at 14.8 min, 16.4 min, 17.9 min, 19.4 min, and 20.7 min attributed to C₁₄-, C₁₅-, C₁₆-, C₁₇-, and C₁₈-alkanes, respectively. The compound eluting at 20.6 min is the anthracene-d₁₀ internal standard which is added prior to GC/MS analysis. No measurable components in Plant B119C were detected in excess of the hydrocarbon contamination present in the blank.

C.13.3.4 Plant B141S--

Figure C.13-8 shows the HPLC chromatogram of the methylene chloride extract of Plant B141S effluent with the five fractions indicated. The approximate Log P range of the components in the fractions were:

<u>Fraction</u>	<u>Approximate log P range</u>
1	3.2 to 3.4
2	3.4 to 4.5
3	4.5 to 5.5
4	5.7 to 5.8
5	6.8 to 6.9

Figure C.13-9 compares the total ion chromatograms obtained from the analysis of the five fractions of the Plant B141S extract. Only fractions 1 and 2 contained measurable components in excess of the impurities present in these extracts.

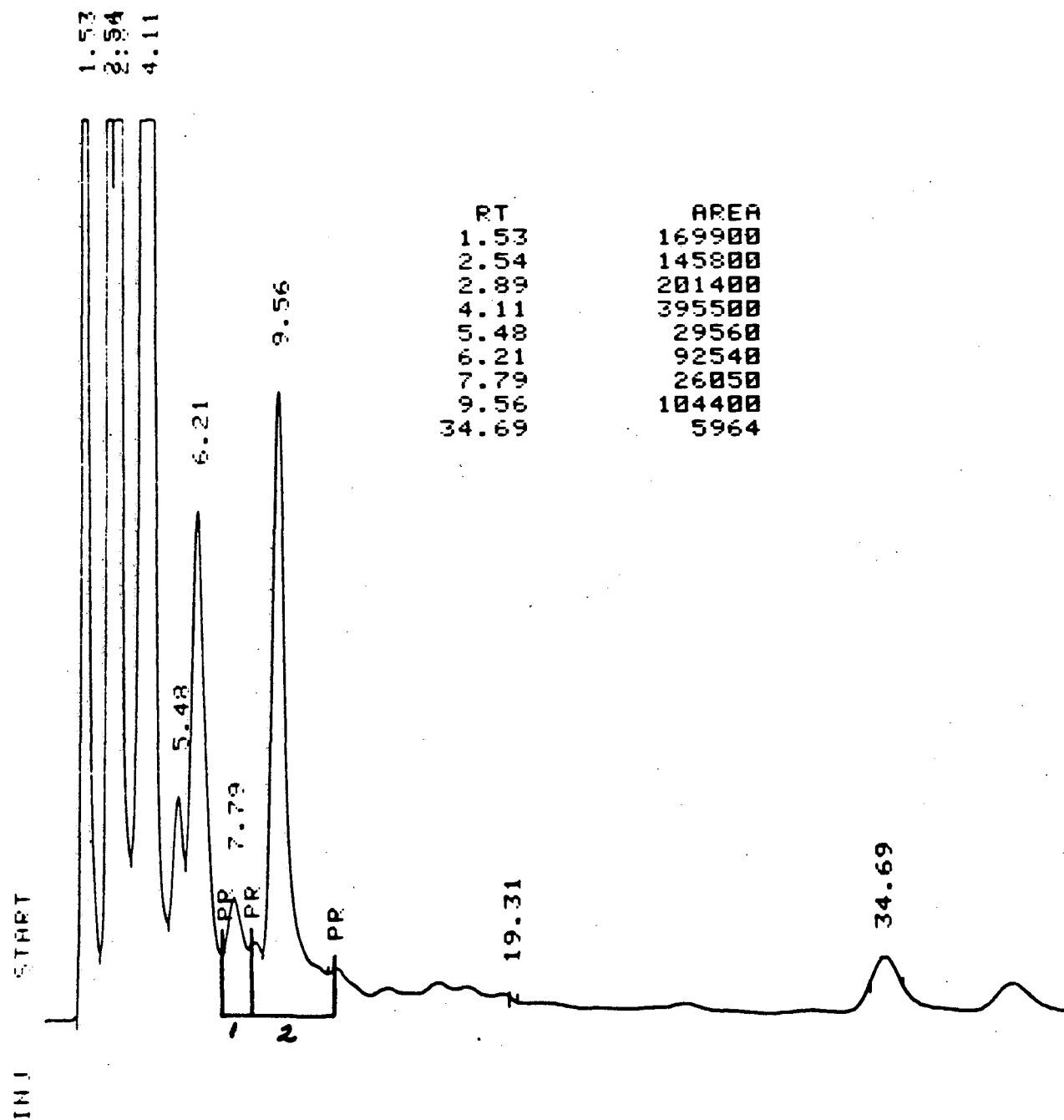


Figure C.13-6. HPLC chromatogram of extract of effluent B119D.

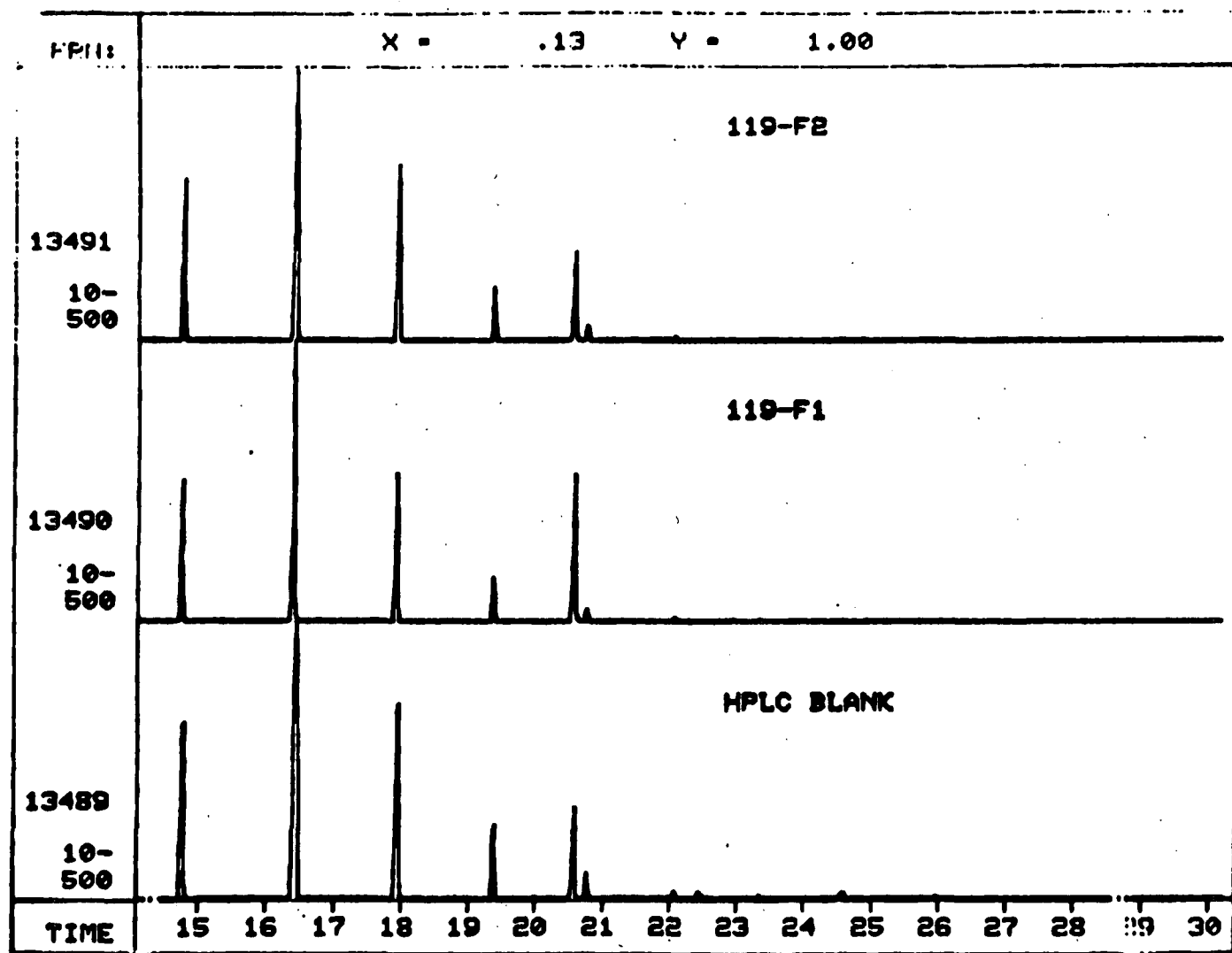


Figure C.13-7. Comparison of the total ion chromatograms obtained from two fractions of the bioaccumulation extract of effluent B119C with an HPLC method blank.

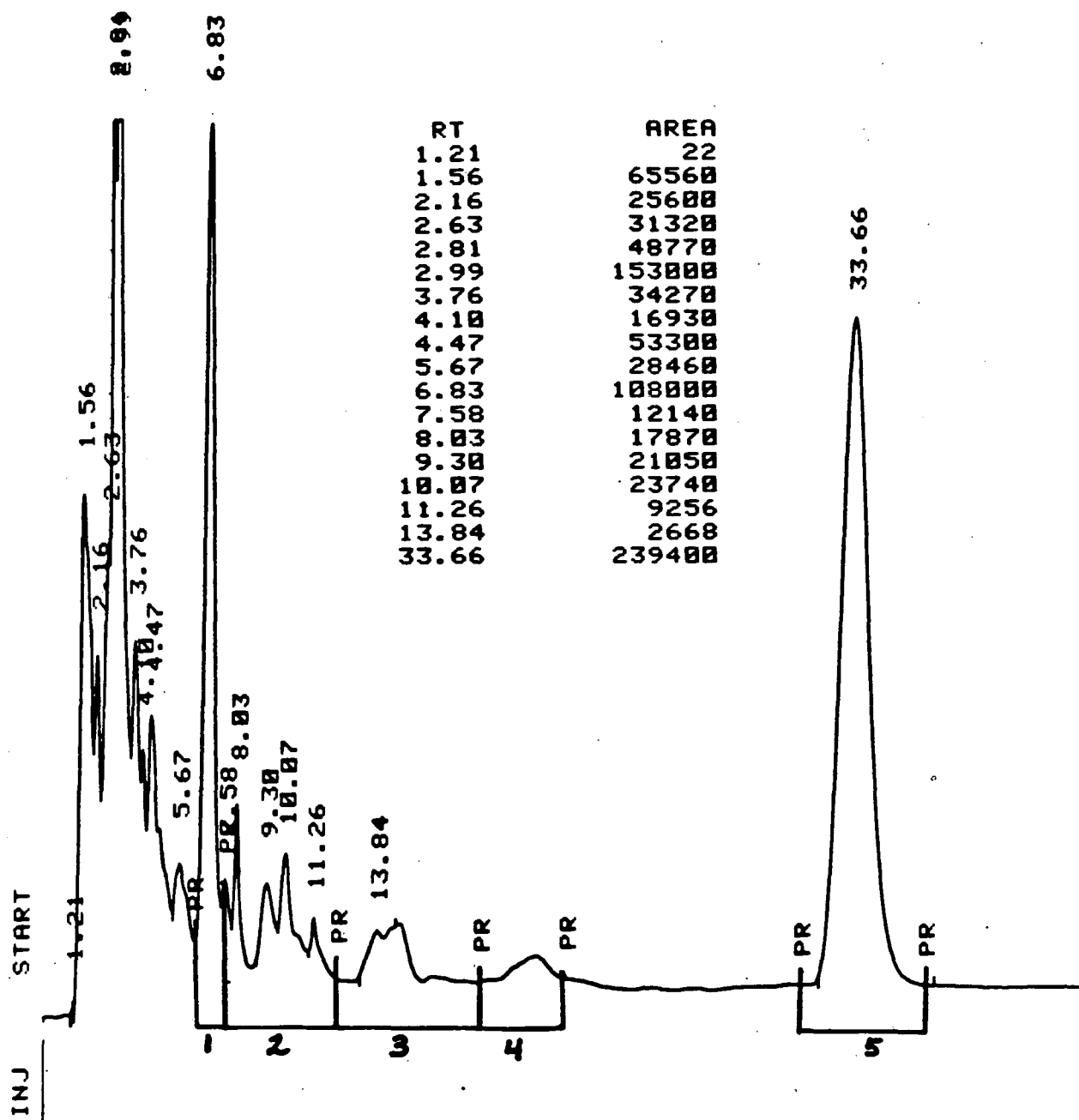


Figure C.13-8. HPLC chromatogram of extract of effluent B141S.

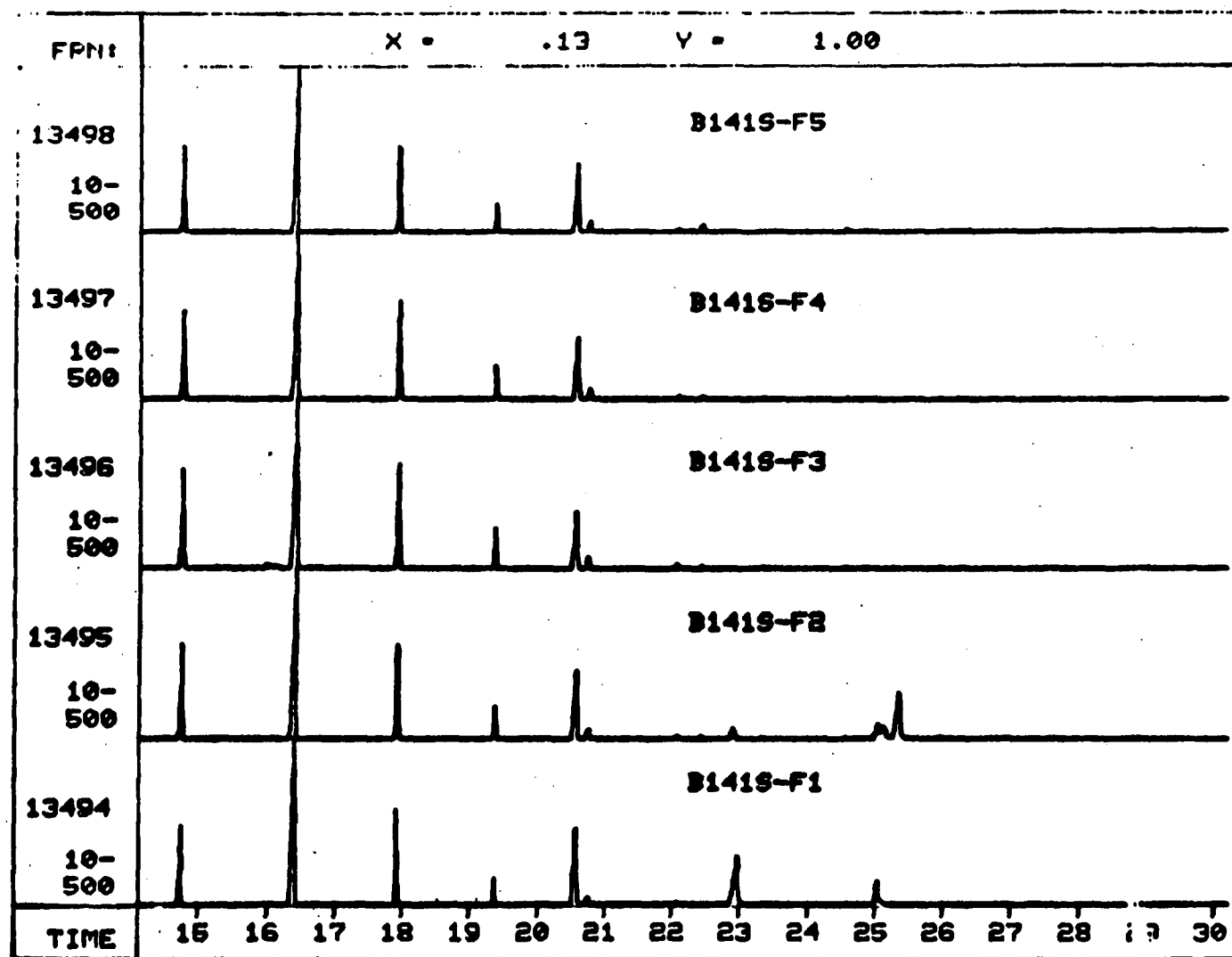


Figure C.13-9. Comparison of total ion chromatograms obtained from five fractions of the bioaccumulation extract of effluent B141S.

Figures C.13-10 to C.13-13 compare mass spectra of the four components from Plant B141S extracts with compounds producing similar mass spectra in the EPA/NIH mass spectral library. Only the component eluting at 22.9 minutes in the first fraction produced a mass spectrum (Figure C.13-10) which agreed well with a library spectrum. This component was identified as hexadecanoic acid. The spectra shown in Figures C.13-11 and C.13-12 appear to be of alcohols and the spectrum shown in Figure C.13-13 appears to be similar to that identified as hexadecanoic acid. Therefore, it is probably also a carboxylic acid.

C.13.3.5 Plant B150D--

Figure C.13-14 shows the HPLC chromatogram of the methylene chloride extract of Plant B150D effluent with the two fractions indicated. The approximate Log P range of the components in the fractions were:

<u>Fraction</u>	<u>Approximate log P range</u>
1	3.5 to 3.6
2	4.2 to 4.3

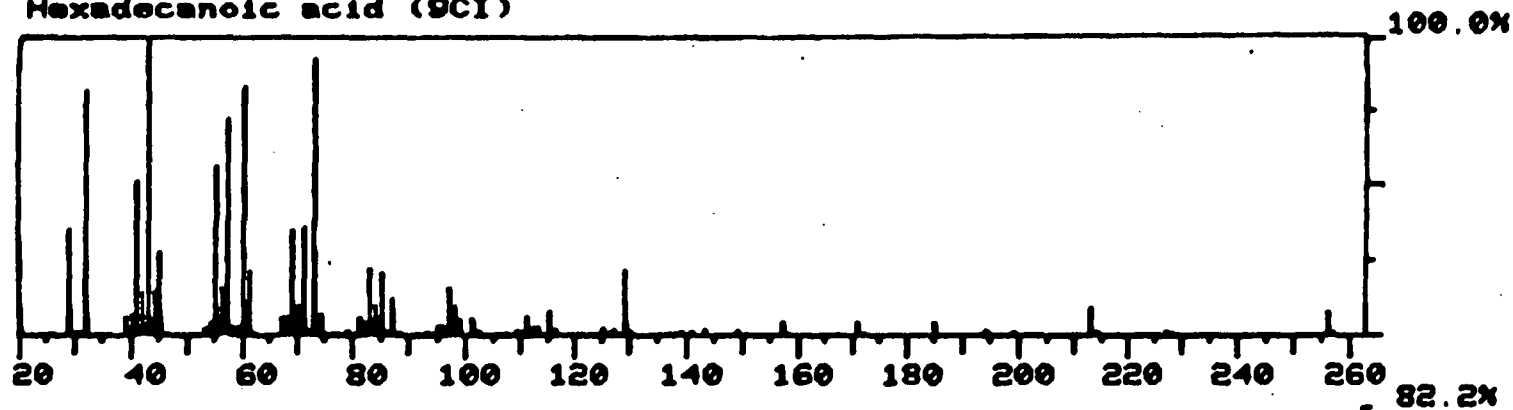
Figure C.13-15 compares the total ion chromatograms from two fractions of the bioaccumulation extract of Plant C150D with an HPLC method blank. The mass spectra of the components in Plants B141S and C150D fractions were the same for both sets of extracts.

C.13.3.6 Plant C161D--

Figure C.13-16 shows the HPLC chromatogram of the methylene chloride extract of Plant C161D effluent with the two fractions indicated. The approximate Log P values of the components in the fractions were:

<u>Fraction</u>	<u>Approximate log P range</u>
1	3.4 to 3.6
2	6.7 to 6.8

FRN 3010 SPECTRUM 2930 MU- 256 C16H32O2
Hexadecanoic acid (9CI)



FRN 13495 SPECTRUM 2191 RET. TIME: 22.9
1 UL 150/150 D10 + B141S-A-F2 9/23/81 BMH

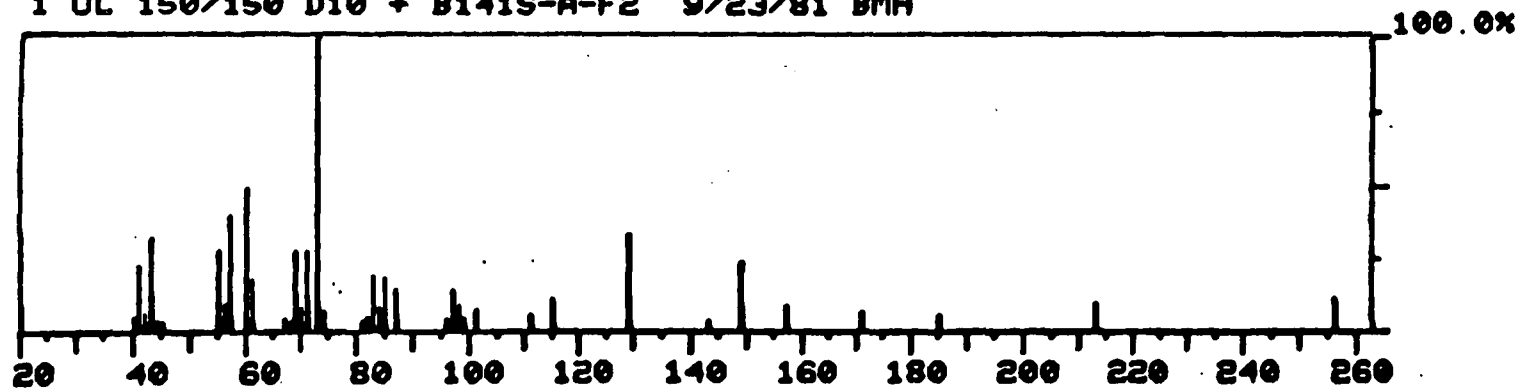
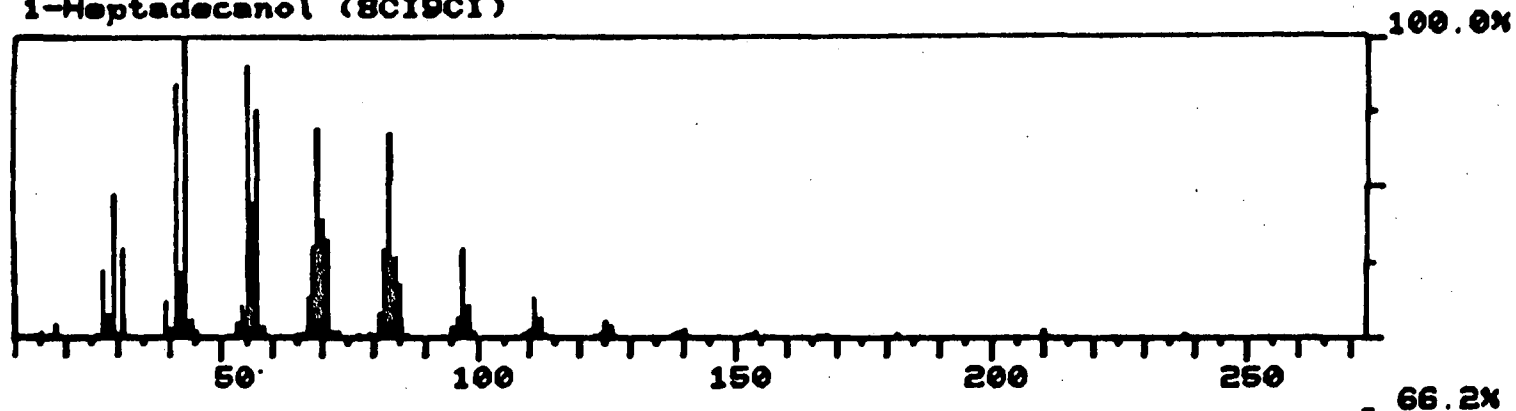


Figure C.13-10. Comparison of the mass spectrum of the compound eluting at 22.9 minutes, present in the first fraction of the bioaccumulation extract of effluent B141S, with that of hexadecanoic acid.

FRN 3010 SPECTRUM 2944 MW= 256 C17H36O
1-Heptadecanol (8C19C1)



FRN 13495 SPECTRUM 2428 RET. TIME: 25.0
1 UL 150/150 D10 + B141S-A-F2 9/23/81 BMH

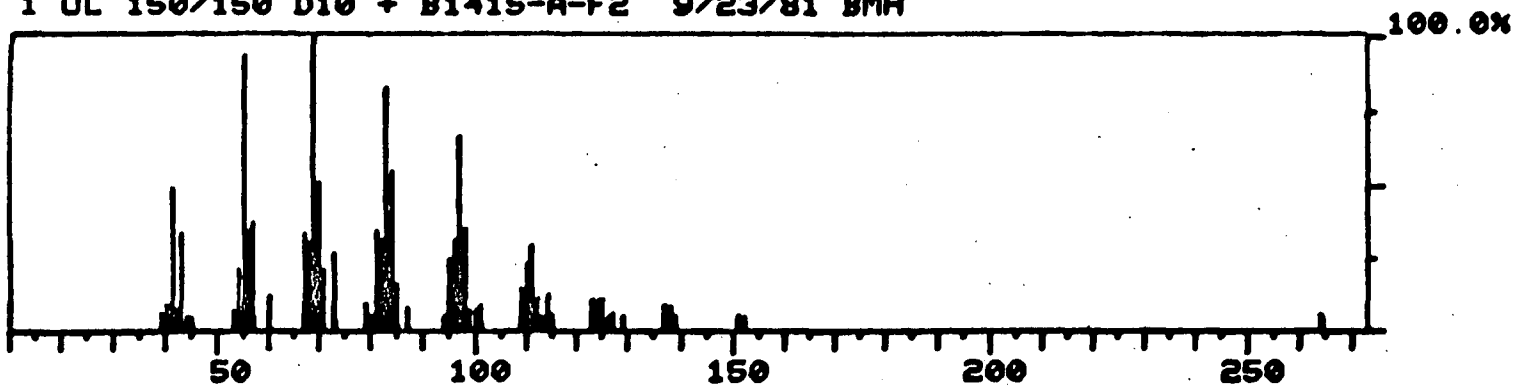
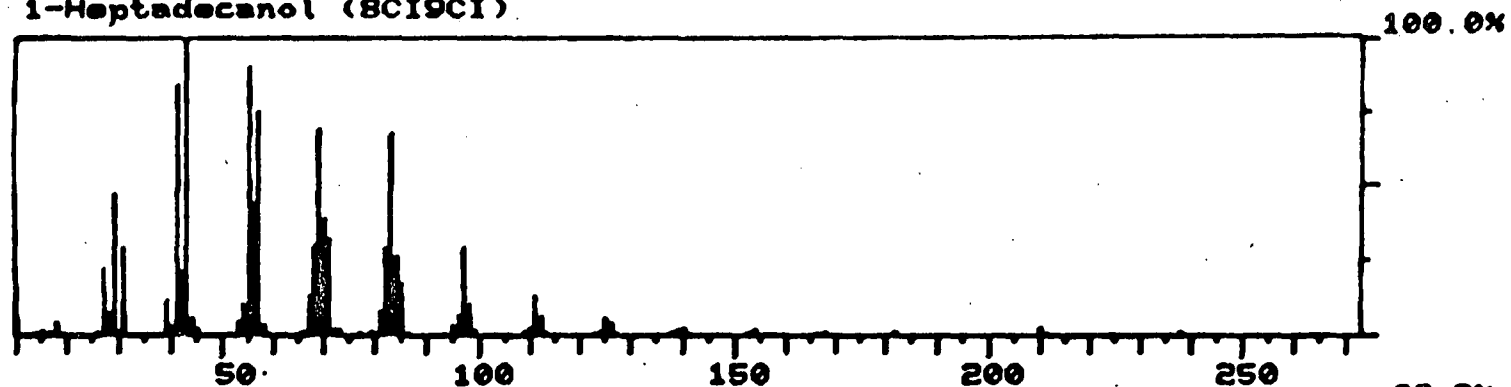


Figure C.13-11. Comparison of the mass spectrum of the compound eluting at 25.0 minutes, present in the first fraction of the bioaccumulation extract of effluent B141S, with that of 1-heptadecanol.

FRN 3010 SPECTRUM 2944 MW= 256 C17H36O
1-Heptadecanol (8CI9CI)



FRN 13495 SPECTRUM 2438 RET. TIME: 25.2
1 UL 150/150 D10 + B141S-A-F2 9/23/81 BMH

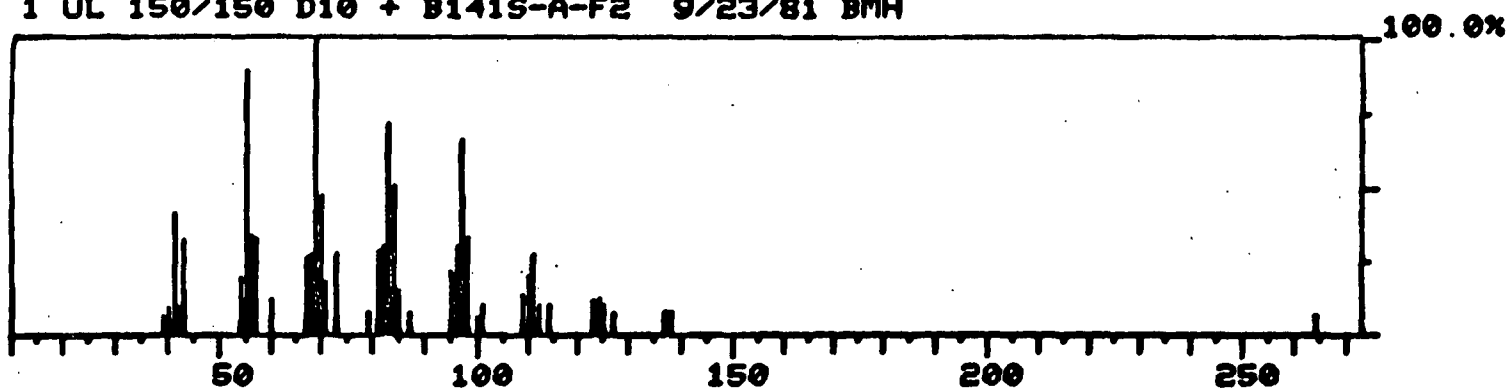
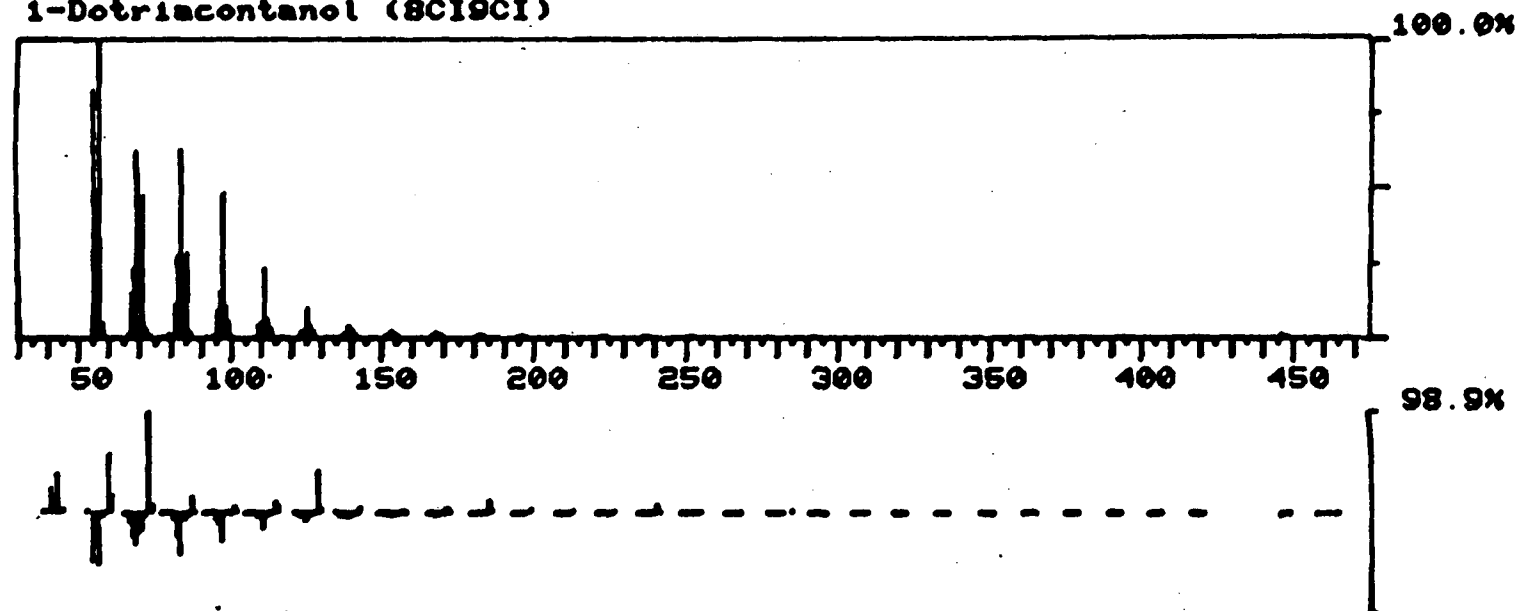


Figure C.13-12. Comparison of the mass spectrum of the compound eluting at 25.2 minutes, present in the second fraction of the bioaccumulation extract of effluent B141S, with that of 1-heptadecanol.

FRN 3019 SPECTRUM 1314 MU- 466 C32H66O
1-Dotriacontanol (8CI9CI)



FRN 13495 SPECTRUM 2462 RET. TIME: 25.4
1 UL 150/150 D10 + B141S-A-F2 9/23/81 BMH

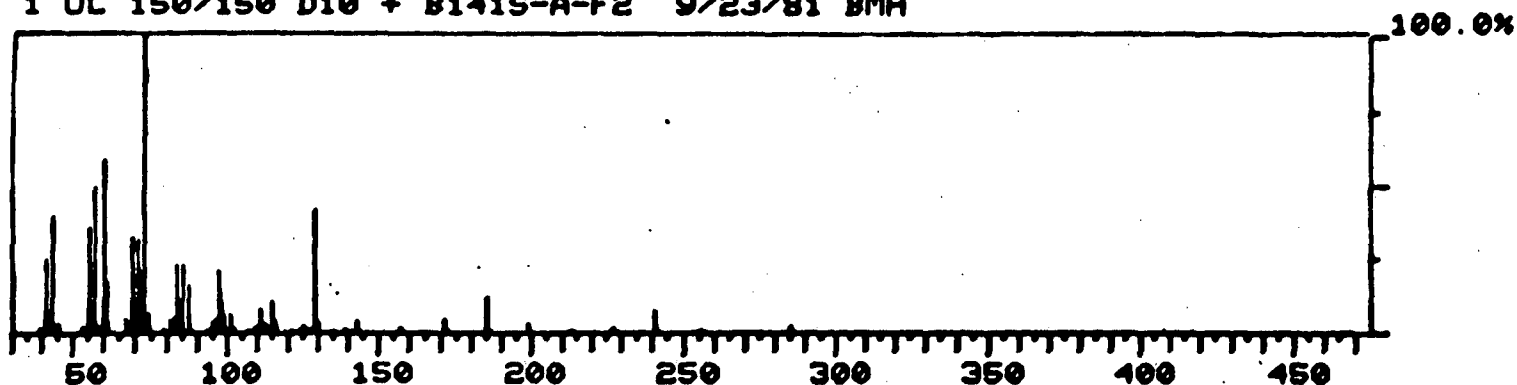


Figure C.13-13. Comparison of the mass spectrum of the compound eluting at 25.4 minutes, present in the second fraction of the bioaccumulation extract of effluent B141S, with that of 1-dotriacontanol.

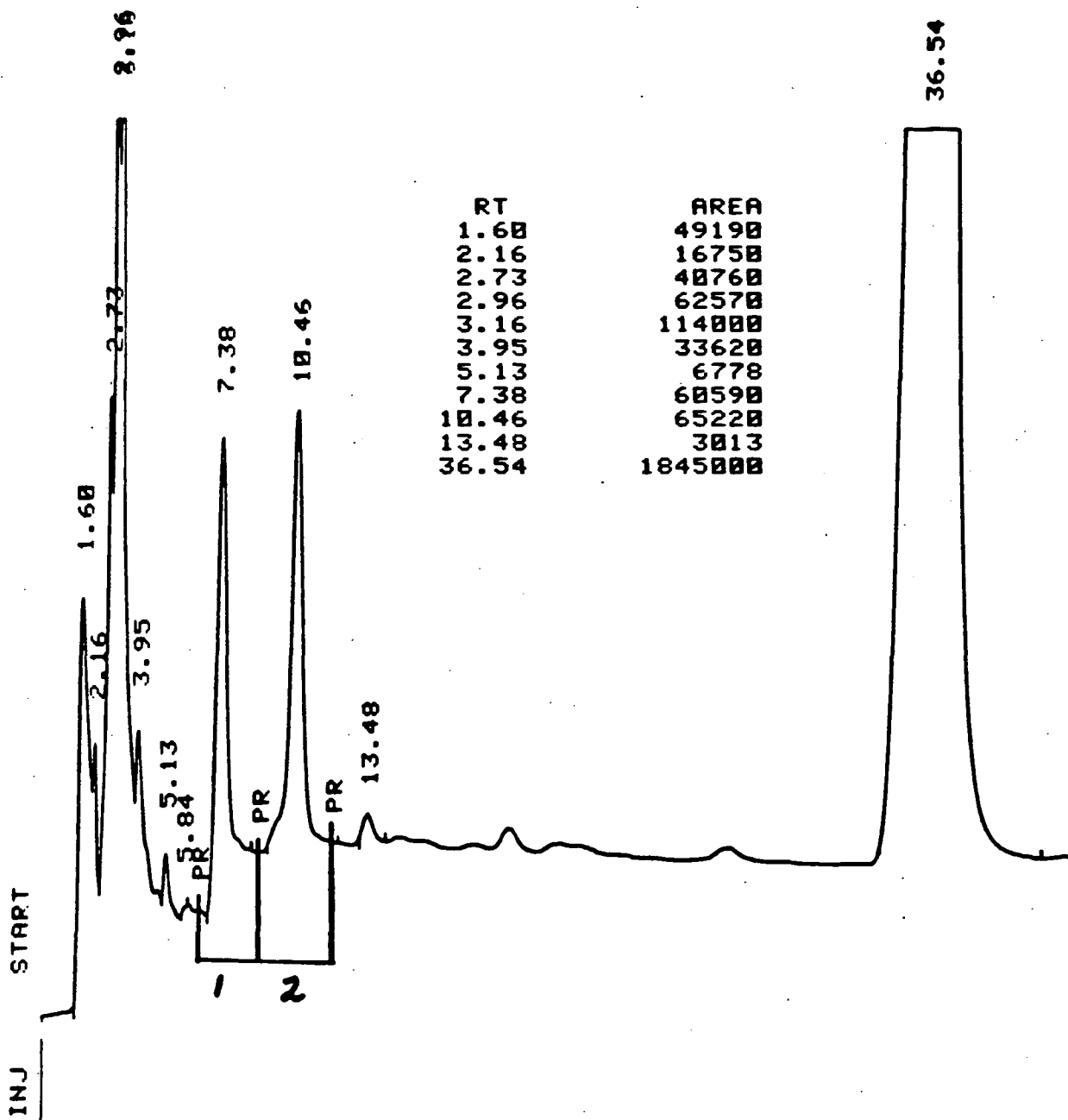


Figure C.13-14. HPLC chromatogram of extract of effluent C150D.

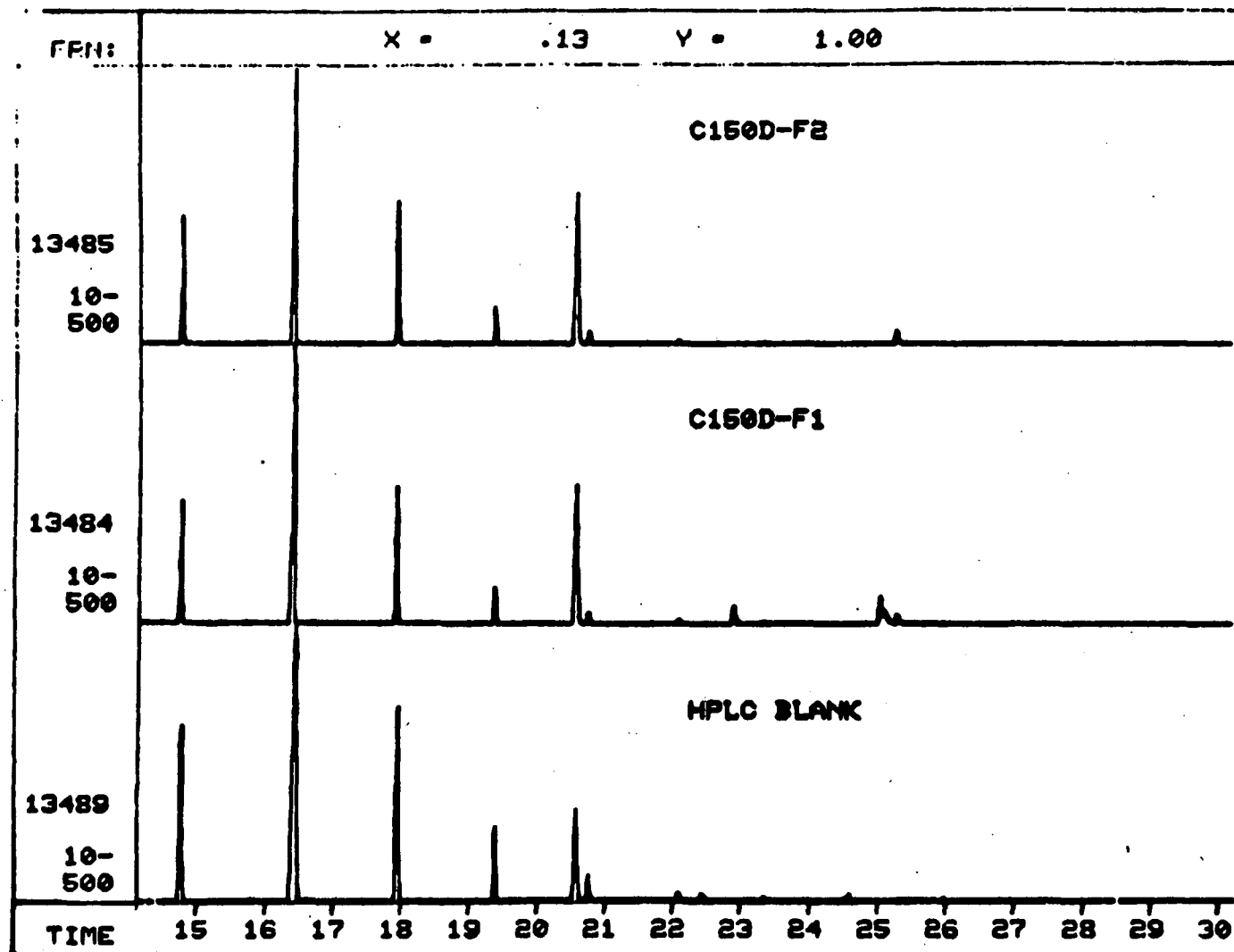


Figure C.13-15. Comparison of the total ion chromatograms from two fractions of the bioaccumulation extract of effluent C150D with an HPLC method blank.

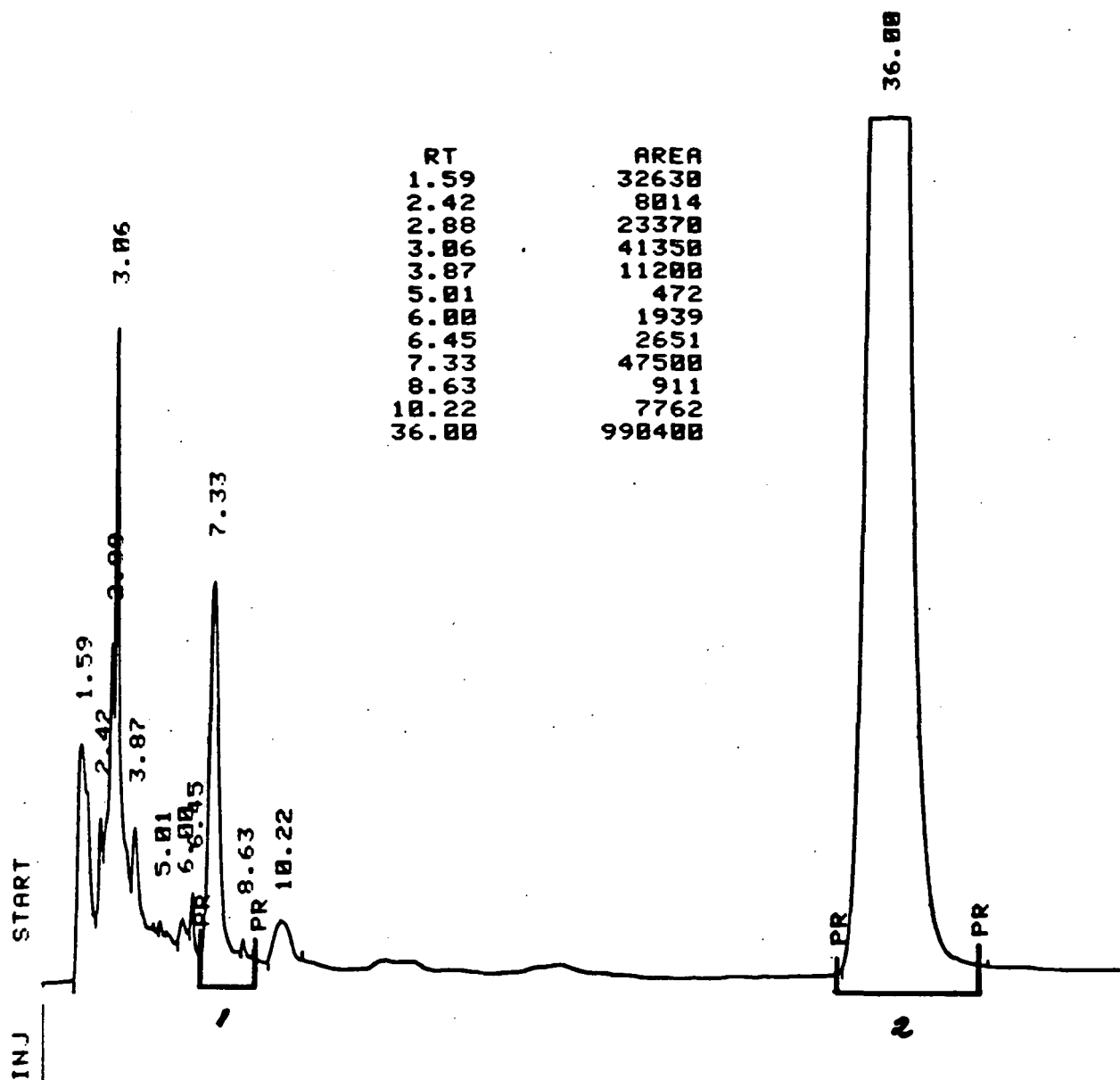


Figure C.13-16. HPLC chromatogram of extract of effluent C161D.

Figure C.13-17 compares the total ion chromatograms obtained from two fractions of the bioaccumulation extract of Plant C161D. The mass spectrum (Figure C.13-18) of the compound eluting at 25.3 minutes present in the first fraction agrees with hexadecanoic acid (Figure C.13-10).

Fraction 2 showed no compounds present other than those found in the method blank. This could be explained by a) the components have a very large UV absorption at 254 nm giving an inaccurate indication of the actual amount of material present, or b) the component is not gas chromatographable.

C.13.4 Conclusion

From the capillary GC/MS analyses of base/neutral and acid extracts shown in Appendix D, it is concluded that long chain fatty acids or high molecular weight alcohols, are probably not the components which are being measured in the bioaccumulation fractions from Plants C150D, C161D, and B141S. Since the levels of total organics present in these three plant extracts, as measured using capillary GC/MS analysis techniques, are approximately one order of magnitude less than those levels measured for the extracts of Plants B112D and B149S, and these latter plants showed only barely detectable components in excess of the large hydrocarbon interferences present in the various extracts, there appears to be inadequate levels of detection for these lower concentrations of components in plant extracts.

The results, however, for Plant B149S show the feasibility of identifying major components which may be detected in the bioaccumulation analysis of water extracts. However, the sensitivity for this overall procedure is not very high. Both the results from the direct capillary GC/MS analysis of the diluted plant extract and of the fractionated plant extracts indicate that there is approximately 400 µg/L methyl naphthalene isomers and

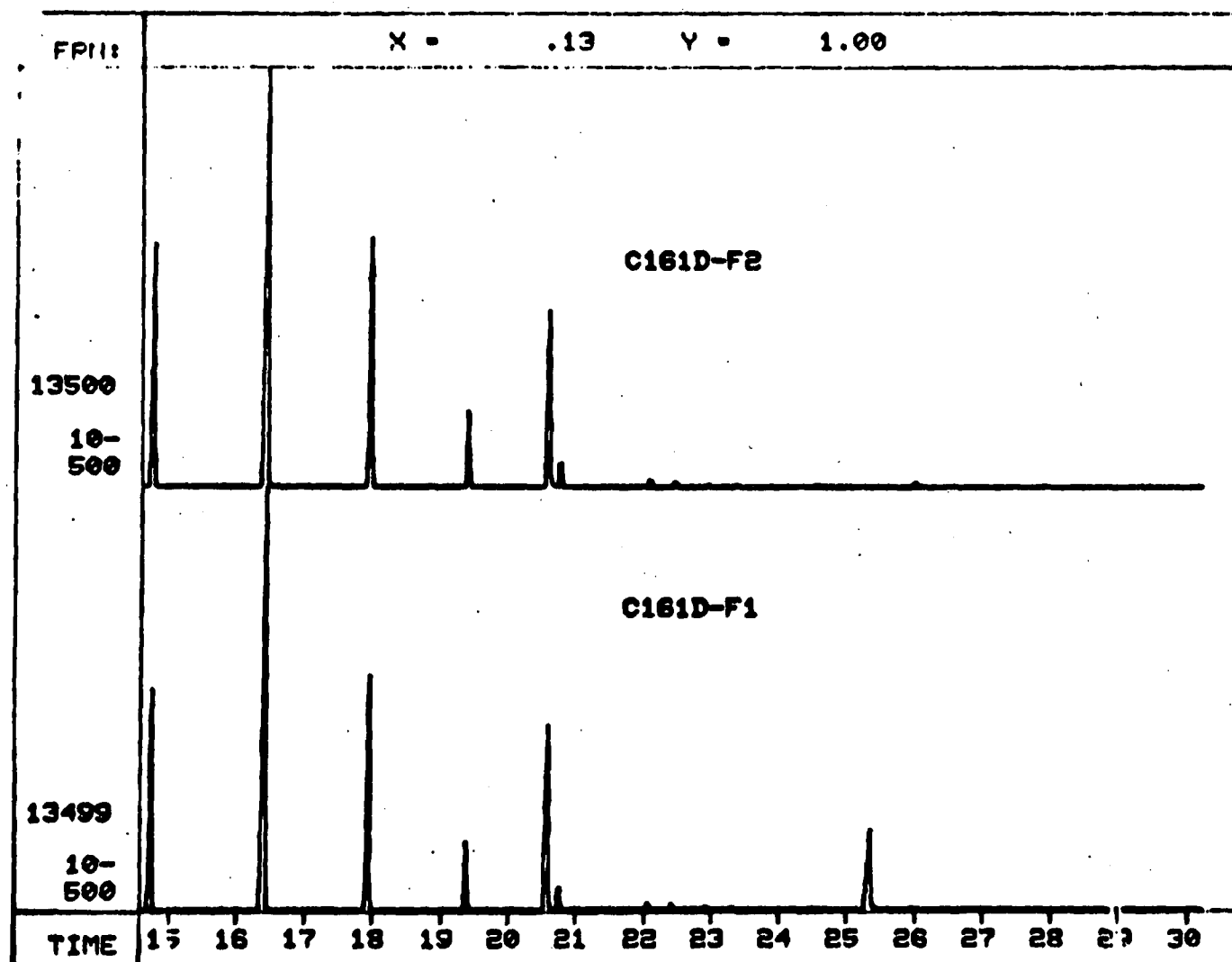


Figure C.13-17. Comparison of total ion chromatograms obtained from two fractions of the bioaccumulation extract of effluent C161D.

FRN 13499	SPECTRUM 2461	RETENTION TIME 25.3
LARGST 4: 73.3, 100.0	60.3, 51.1	57.3, 42.5 129.3, 38.1
LMST 4: 227.5, 2.0	241.5, 7.1	284.7, 11.0 285.7, 1.7
		PAGE 1 Y = 1.00

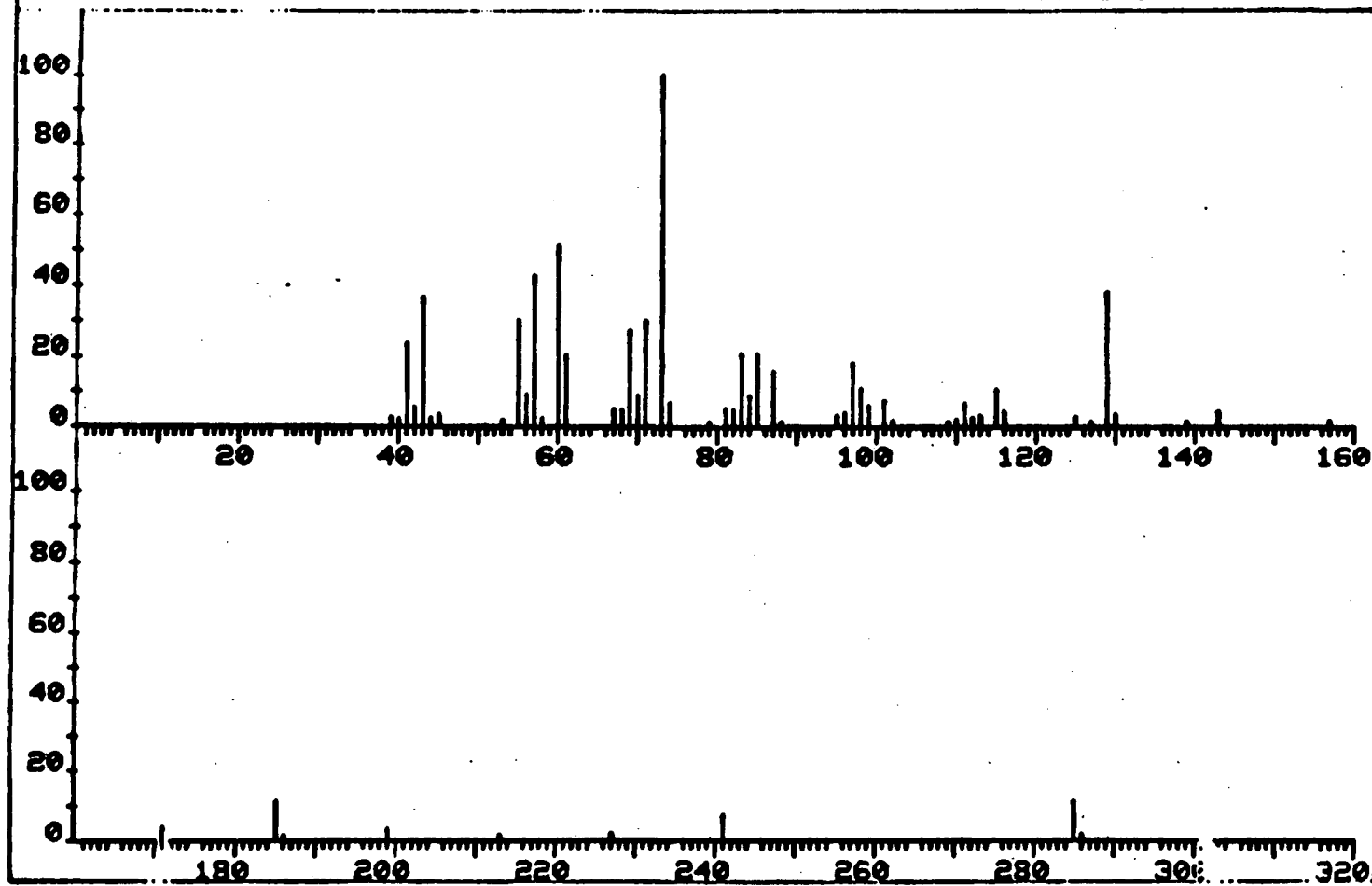


Figure C.13-18. Mass spectrum of compound eluting at 25.3 minutes present in the first fraction of the bioaccumulation extract of effluent C161D.

C.13-28

600 µg/L dimethyl naphthalene isomers. The limit of detection for components in the fractionated sample is approximately one order of magnitude below this level. However, the large impurities in the solvents, and the limited amount of sample which can be fractionated in a reasonable period of time, result in this analytical technique only being applicable to gross components of a water extract. If the capillary GC/MS analysis of the original plant effluent extract were conducted for a defined group of suspected bioaccumulating compounds, levels of detection for compounds such as PAHs and PCBs would be on the order of 1 µg/L. Thus, this latter approach is more applicable to bioaccumulating compounds which need to be detected in the low- or even sub-ppb range.

C.14 AQUATIC TOXICITY ANALYSES OF EFFLUENTS

C.14.1 Mysid Shrimp Assay

Marine toxicity tests were conducted at E.G.&G. Bionomics Marine Research Laboratory (BMRL), Pensacola, Florida, to determine the acute effect on mysid shrimp *Mysidopsis bahia* of effluent samples collected in the Chesapeake Bay area. Eight samples were collected from the State of Maryland and 10 samples from the State of Virginia. Of the 10 samples collected in the State of Virginia the toxicity of those from Plants A109, B119D, and C161D was also evaluated using fathead minnows as described in Section C.14.2.

C.14.1.1 Sample Collection and Shipping--

At each site a 10-gallon (38-liter) sample was collected in 5-gallon polypropylene cubitainers. Following collection, samples were packed in ice and shipped to BMRL via air freight. Upon receipt at the BMRL facility, samples were stored at 4°C until the bioassay testing was started.

C.14.1.2 Experimental Methods--

Methods for the 96-hour static tests were based on those given in "IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)" [27]. The criterion for toxic effect was death of the shrimp, and test results are expressed as 24-, 48-, 72-, and 96-hour LC₅₀ effluent concentration (the concentration of sample estimated to be lethal to 50% of the test organisms at the specified exposure duration).

[27] Lentzen, D., D. Wagoner, E. Estes, and W. Gutknecht. IERL-RTP Procedures Manual: Level 1 Assessment (Second Edition). EPA-600/7-78-201, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978.

Juvenile mysids were isolated from adults and were acclimated in flowing, natural seawater until testing was initiated. The animals were estimated to be six to nine days old at test initiation and appeared to be in excellent condition.

Twenty-four hours prior to testing, the salinity of each effluent was adjusted with Rila Marine Mix to a salinity that was approximately that in which test animals were being cultured and maintained. Artificial seawater used in control tanks and for dilution was deionized water containing an amount of Rila Marine Mix equivalent to the amount that had been added to the effluent sample. It was prepared 24 hours prior to test initiation.

Shrimp were definitively tested at nominal effluent concentrations of 3% to 100% (expressed a percentage of effluent in artificial seawater on a volume/volume basis). Test concentrations were prepared by adding appropriate volumes of effluent to each test container and diluting to the appropriate concentration with artificial seawater. A Rila Marine Mix control was also prepared by adding an equivalent amount of salts to deionized water as had been added to each effluent sample for purposes of salinity adjustment.

Toxicity tests were conducted in one-liter covered glass beakers, each of which contained one liter of test solution or control (artificial) seawater. Test solution temperature was maintained at $22 \pm 1^{\circ}\text{C}$, and aeration was not provided. Five animals were tested per jar.

C.14.1.3 Quality Control/Quality Assurance Aspects--

For purposes of evaluating effluent toxicity data quality, all tests were run in triplicate. In addition, control beakers were used, each containing 100% artificial seawater.

C.14.1.4 LC₅₀ Calculation--

When data were amenable, LC₅₀ values and their 95% confidence limits were calculated by digital computer. The computer program estimated LC₅₀ values by one of three statistical techniques in the following order: moving average angle analysis, probit analysis, or binomial probability. The method selected was determined by the characteristics of the data, with the presence or absence of 0% and 100% shrimp mortality and the number of concentrations in which mortality between 0% and 100% occurred serving as criterion for selection [28]. The computer scanned the data, identified the most suitable method, and performed the required calculations.

C.14.2 Fish Assay (Fathead and Sheepshead Minnows)

Effluent samples from 13 industrial operations or sewage treatment plants in the Chesapeake Bay area of Virginia were collected and transported to the State Water Control Board's (SWCB) bioassay facility in Richmond. Tests were conducted on 12 of the effluents to estimate their acute toxicity to fathead minnows, while the toxicity of the remaining effluent stream (Plant C153D) was estimated using sheepshead minnows as the test species. In addition, the toxicity of three of these effluents (Plants A109, B119D, and C161D) was also evaluated using the mysid shrimp assay procedure described previously in Section C.14.1.

C.14.2.1 Sample Collection and Shipping--

At each site a 110-gallon (416-liter) sample was collected and stored in upright 55-gallon (208-liter) tanks constructed of linear polyethylene. After collection and during storage, these tanks were sealed to prevent loss of volatile components from the

[28] Stephan, C. E. Methods for Calculating an LC₅₀, ASTM, Aquatic Toxicology and Hazard Evaluation. ASTM STP 634, F. L. Mayer and J. L. Hamclink, eds., 1977.

samples. A submersible pump was used to fill each sample container, and all connective tubing was polyethylene-lined plastic (VEV-A-LINE V-HT®). Due to relatively short transport times and potential experimental problems associated with rewarming the effluent sample to the test fish acclimation temperature, samples were not refrigerated during transport to Richmond or subsequent storage.

The duration between sample collection and start of bioassay testing was usually less than three hours. To eliminate potential toxic effects due to the presence of residual chlorine, chlorinated samples were aerated for 24 to 48 hours, until total chlorine residual was 0.1 mg/L or less. One chlorinated sewage effluent sample was tested immediately upon receipt at the SWCB facility.

C.14.2.2 Experimental Methods--

The detailed basis for the fish toxicity testing methods can be found in "Methods for Acute Toxicity Tests with Fish, Macroinvertebrates and Amphibians" [29] and "Methods for Measuring the Acute Toxicity of Effluents to Aquatic Organisms" [30]. A 96-hour static test was employed with the following modification: after 48 hours of test species exposure, the test solutions were renewed using an aliquot of the initial 110-gallon sample.

The test fish species for all effluents except Plant C153D was the fathead minnow, *Pimephales promelas*. Because of the salinity of sample C153D, a brackish water species, the sheepshead minnow, *Cyprinodon variegatus*, was used. Fathead minnows were obtained

[29] Stephen, C. E. Methods for Acute Toxicity Tests with Fish, Macroinvertebrates and Amphibians. EPA-600/3-75-009, U.S. Environmental Protection Agency, 1975.

[30] Peltier, W. Methods of Measuring the Acute Toxicity of Effluents to Aquatic Organisms. EPA-600/4-78-D12, U.S. Environmental Protection Agency, 1978.

from Kurtz's Fish Hatchery, Elverson, Pennsylvania, and acclimated in the test dilution water at the SWCB bioassay facility. The sheepshead minnows were captured, wild stock, from a tidal creek on Virginia's Eastern Shore (Accomack County). Batches of fish were treated for specific pathogens only when necessary; no general prophylaxis was administered. All fish appeared healthy, and previous observed mortality rates were well within tolerances when the tests were begun.

Fathead minnows were held in continuous-flow 135-gallon (500-liter) fiberglass raceways prior to the tests. The water supply to these raceways and also that used to make all test dilutions was tap water obtained from the City of Richmond Public Utilities. Prior to use in the holding tanks, this water was treated with carbon filtration, ultraviolet light, and diffused air.

Sheepshead minnows were held in a recirculating, salt-water holding tank system having a salinity of 14,000 mg/L. This salinity was subsequently lowered to 11,000 mg/L shortly before the effluent test to more closely match the salinity of effluent sample C153D. Holding tank water was also used to make test dilutions.

Test vessels were all-glass, 10-gallon (38-liter) commercially available aquaria. The following cleaning procedure was used on these aquaria before the initial test and between each subsequent test:

1. Submerge and scrub aquarium in a 2% solution of Micro-wash®, a commercially available liquid detergent.
2. Allow aquarium to soak overnight in Microwash® solution.
3. Rinse aquarium thoroughly for several minutes with running dilution water.
4. Rinse aquarium thoroughly, for several minutes, with running laboratory deionized water and repeat.
5. Invert to drain and dry.

A similar procedure was used to clean all glassware, tubing, pumps, and other tanks used throughout the test series.

No fish screening tests were performed with the test species. Instead, 96-hour static effluent tests were immediately initiated upon receipt of the 110-gallon effluent sample from the field. Each tank was loaded with ten randomly-selected fish. Five effluent sample concentrations (10, 18, 32, 56, and 100%) were tested.

Dissolved oxygen, pH, and temperature in each holding tank were measured initially and at 24-hour intervals through completion of the testing. A YSI Model 57 D.O. meter was used to measure dissolved oxygen and temperature; this meter was calibrated daily for dissolved oxygen versus the Winkler method (azide modification). The meter's temperature function was compared with a mercury-filled laboratory thermometer.

pH measurements were made with a Corning Model 610A pH meter, which was calibrated daily using two buffers, one having a pH of 4.0 and one of 7.0.

C.14.2.3 Quality Control/Quality Assurance Aspects--

As a means of evaluating the quality of the effluent toxicity data, all tests were run in duplicate. In addition, two control tanks were used, each containing 100% dilution water. Thus, a total of 12 tanks and 120 fish were used for each sample tested.

C.14.2.4 96-Hour LC₅₀ Concentration--

Dead fish were counted and removed from each holding tank at 24-hour intervals during the test duration. Data analysis was accomplished using a log-probability graphical technique. The fraction of test fish which had died after 96 hours of exposure was plotted on the probability scale versus the effluent sample concentration (expressed as percent by volume) on the logarithmic scale. These points were connected by straight lines and the -

effluent concentration which would kill 50% of the test organisms was read from the graph. This value is defined as the 96-hour LC_{50} (lethal concentration).

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