ASSESSMENT OF MISSOURI RIVER HABITAT QUALITY WITH SEMIPERMEABLE MEMBRANE DEVICES (SPMDs)

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SUMMARY

The semipermeable membrane device (SPMD) technology [developed at and patented by the National Fisheries Contaminant Research Center (NFCRC)] was used to define the presence of organic contaminants in the main stem of the Missouri River. Specifically, the SPMDs were deployed at five sites - Sioux City, IA; Nebraska City, NE; Kansas City, MO; Glasgow, MO; and Hermann, MO - for a period of 28 days. The SPMDs and associated containment cages were prepared at NFCRC. The SPMDs were deployed and retrieved through the joint efforts of NFCRC and Columbia ES office personnel. Following retrieval of the SPMDs, the devices were processed and the extracts analyzed for organochlorine pesticide (OC), polyaromatic hydrocarbon (PAH), and polychlorinated biphenyl (PCB) residues. Over 400 analyses were performed on samples from the five deployment sites. In general, OCs were detected at all sites, PAHs at Nebraska City, Kansas City and Glasgow with PCBs being at essentially background levels at all sites. Residues sequestered in replicate SPMD samples were very reproducible (C.V. 10 - 35%) and represent an estimation of the bioavailable organic contaminants present in the main stem of the Missouri River. Based on the contaminants identified, the five sites can be ranked in terms of pollution severity - from lowest to highest - as follows: Sioux City, Nebraska City, Kansas City, Hermann, Glasgow. Incidentally, the Kansas City site was above the metropolitan Kansas City area and is not indicative of the pollution input from Kansas City. The second year of this study was designed to ascertain the pollution input from major tributary streams. Unfortunately, the second year funding was canceled.

I. INTRODUCTION

Economic and agricultural expansion in the Missouri River Basin has led to extensive losses of historic fish and wildlife habitats over the last 50 years. Activities such as channelization and agricultural conversion have eliminated over 40,000 acres of Missouri River aquatic habitat; concomitantly, over 375,000 acres of wetland and terrestrial habitat have been drained and cleared. Thus, nearly 95% of riverine wetland habitat has been lost, which has led to significant declines of wetland-dependent fish and wildlife. We now recognize that wetland losses have occurred at significant cost to society, as riparian wetlands perform numerous critical ecological functions: provision of habitat and nursery grounds for fish and wildlife; nutrient and contaminant retention; water quality improvement; groundwater recharge; and amelioration of flooding via storm-water retention.

Thus, reduction of wetland habitat has led to significant losses of benefits to society. Recognition of these losses resulted in passage of the Water Resources and Development Act of 1986. This act seeks to mitigate the losses of Missouri River habitat by acquisition, restoration, and protection of riverine and riparian fish and wildlife habitats. Numerous interests, including the U.S. Fish and Wildlife Service, the U.S. Army Corps of Engineers, the Tribes, and State

Governments have opportunities to interact in partnerships to mitigate losses of habitats in the Missouri River and its Basin.

Successful restoration of fisheries and wetlands in the Missouri River Basin will require a comprehensive assessment of environmental contaminant issues. Contaminants such as chlordane and PCB's have led to consumption advisories on sturgeon, paddlefish, and catfish, thus diminishing the aesthetic, recreational, and commercial value of a multi-million dollar fishery. Further, organochlorine residues from past insecticidal usage have been implicated in mortality of endangered species of bats and shorebirds.

Knowledge of the types and amounts of biologically available trace contaminants in environmental waters is a fundamental part of assessing the overall health of ecosystems. Unfortunately, these key environmental concentration data are often unavailable to resource managers and regulators because of the transient nature of most chemical spills and pesticide applications, and the limited ability of analytical laboratories to detect very low levels of persistent contaminants in water. Also, unlike air monitoring technology, few methods exist to passively determine time-weighted average contaminant concentration, i.e. environmental dosimetry, in aquatic systems.

Researchers at the National Fisheries Contaminant Research Center at Columbia, Missouri have developed an in-situ water sampling device (subject of a government patent) that mimics the bioconcentration of organic contaminants in lipids of aquatic organisms. The sampler operates passively and consists of a thin film of neutral lipid enclosed in a layflat semipermeable membrane tube. The high membrane surface area-to-lipid-volume ratio of the device permits contaminant (e.g. PCBs, PAHs, etc.) sampling rates of ca. 4 to 8 L water per g lipid per day (17-25°C) even though so called "nonporous" polymeric films (typically polyethylene) are used for sampler membranes. Unlike living organisms that metabolize and excrete many toxic organic contaminants, often eliminating the causal link between residue concentration and adverse effects, these time-weighted sampling devices appear to continue to concentrate organic pollutants from water to their maximum partitioning limits, which exceeds 10^6 for some analytes. Also, only dissolved biologically available contaminants concentrate in the sampler lipid because of the small size of the cavities through the polymeric membrane. This selectivity contrasts with nearly all currently used water monitoring techniques.

These simple, in-situ devices enable investigators to rapidly and cost-effectively measure the presence and bioavailability of organic contaminants to aquatic organisms such as fish. Further, these devices have significant statistical advantages over traditional contaminant assessments due to ease of use and

interpretation. This report details the results of a project designed to define the presence of environmental contaminants in the main stem of the Missouri River.

II. PROJECT OBJECTIVES

1. Demonstrate the use of SPMDs as a screening tool for the assessment of selected contaminants in the Missouri River System.

2. Provide a relative ranking of the various demonstration sites in regards to the presence of PCBs, PAHs, and OCs.

3. Demonstrate the potential for use of SPMD technology in pre- and post-refuge acquisition surveys, in the development of plans for restoration of endangered species, fisheries, wetlands, in assessment of the hazards of dredge-fill materials and in law enforcement activities in areas where contaminants are an issue.

III. EXPERIMENTAL APPROACH

The SPMD technique was used to determine the relative amounts of hydrophobic organic contaminants in various reaches of the Missouri River. Specifically, SPMDs were placed in the main stem of the Missouri River at five locations.

These five locations; Sioux City, IA, Nebraska City, NE, Kansas City, MO, Glasgow, MO and Hermann, MO are located in proximity to large tributary streams. The SPMDs were placed upstream near the confluence of the tributary stream with the Missouri River. Four replicate SPMDs were deployed at each of the five demonstration sites.

Following a 28-day exposure, the SPMDs (including trip blanks) were recovered and transported to the NFCRC for further processing. SPMD processing and sample enrichment techniques followed revisions of standard operating procedures (SOPs). Analytical determinations were conducted using capillary gas chromatography with electron capture and photoionization detection. Selected samples were examined for unknowns and for confirmation of identified contaminants, using gas chromatography/mass spectrometry.

Samples from all sites were analyzed to determine the presence or absence of the following contaminants:

A. NCBP OCs and PCB's

Hexachlorobenzene (HCB)	o,p'-DDE
Pentachloroanisole (PCA)	p,p'-DDE
α-BHC	Dieldrin

Lindane	o,p'-DDD
β-BHC	Endrin
Heptachlor	Cis-nonachlor
δ-BHC	o,p'-DDT
Aldrin	o,p'-DDD
Dacthal	o,p'-DDT
Oxychlordane	Mirex
Heptachlor Epoxide	Toxaphene
Trans-chlordane	Aroclor 1248
Trans-nonachlor	Aroclor 1254
Cis-Chlordane	Aroclor 1260

B. Priority Pollutant PAHs

Acenaphthene

Acenaphthylene

Anthracene

Benz(a)anthracene

Benzo(a)pyrene

Benzo(b)fluoranthene

Benzo(g,h,i)perylene

Benzo(k)fluoranthene

Chrysene

Dibenz(a,h)anthracene

Fluoranthene

Fluorene

Indeno(1,2,3-c,d)pyrene

Naphthalene

Phenanthrene

Pyrene

Upon completion of the residue analyses, a relative ranking of the demonstration sites was prepared. This ranking may serve as the benchmark for the presence of hydrophobic organic contaminants in the Missouri River. The SPMD approach can serve as a means of defining the presence and potential significance of contaminants in a broad array of fish and wildlife habitats.

IV. QUALITY ASSURANCE/QUALITY CONTROL

This research project was conducted in general accordance with the NFCRC's Quality Assurance guidelines (appropriate sections from: 160.120, 40 CFR Ch.1, 7-1-85, subpart G - "Protocol for and conduct of a study"). A copy of the study protocol is included in the Quality Assurance/Quality Control Appendix. All

original data is archived at the NFCRC. Summary data presented in this report have been reviewed by the authors and NFCRC management.

The Quality Control data for this project are summarized in the Quality Assurance/Quality Control Appendix. The Quality Control parameters (i.e. blanks, control samples, spike recoveries, calibration curves, representative chromatograms etc.) are designed to ensure that the analytical data are a true representation of organic contaminant residues present in SPMDs from the main stem of the Missouri River. All concentration values reported are above the method quantitation limits presented in the Quality Assurance/Quality Control Appendix.

V. RESULTS AND DISCUSSION

The SPMD sampler arrays were successfully deployed at the five sites in the main stem of the Missouri River. The SPMDs were enclosed in stainless steel cages (see diagrams and pertinent SOP contained in SPMD Deployment Appendix). Four replicate SPMD samples (2 individual 152-cm tubes per sample) were contained in each cage. Two cages were deployed at each site to provide redundant samples.

Following a 28-day exposure, the SPMDs were recovered. One cage structure and associated SPMDs (Sioux City, IA site) could not be recovered due to sand/silt build-up. All recovered SPMDs were sealed in air-tight containers, maintained on ice and shipped to the NFCRC for processing and analysis.

The SPMD samples were processed according to the appropriate NFCRC SOP (see Sample Processing and Analysis Appendix). In general, the SPMDs were subjected to a rigorous cleaning procedure to remove adhering periphytic growth and precipitated carbonate salts. Following this cleaning procedure the SPMDs were dialyzed for 48 hours using hexane. The resulting dialysates were subjected to a series of residue enrichment procedures (see flow chart contained in the Sample Processing and Analysis Appendix).

The various fractions resulting from these enrichment procedures were analyzed for residues of OCs, PAHs and PCBs according to the appropriate NFCRC SOP (see Sample Processing and Analysis Appendix). The results of analysis of the four replicate SPMD samples for OC residues at each deployment site is presented in Table 1. An examination of the data presented in Table 1 revels that the level of all OCs increase down river from Sioux City to a maximum at Glasgow, MO before dropping at Hermann, MO.

The concentrations of the chlordane components, heptachlor expoxide, and dieldrin were highest in SPMDs from all sites. The total chlordane components ranged from a high of 566 ng/sample at Glasgow to a low of 17 ng/sample at Sioux City. Heptachlorepoxide was highest at Hermann (170 ng/sample) and lowest at Sioux City (22 ng/sample). The most acutely toxic pesticide (fathead minnow, 96 h LC 50) in this group is dieldrin, which ranged from a high of 810 ng/sample at Glasgow to a low of 64 ng/sample at Sioux City.

The above concentrations of OC's are not unexpected considering the extensive use of chlordane, dieldrin and heptachlor (heptachlor epoxide is a breakdown product of heptachlor) in agriculture and for termite control. However, the presence of toxaphene residues in all sampling devices (ranging from 880 ng/sample at Glasgow to 100 ng/sample at Sioux City) was unexpected. The chromatographic pattern of the toxaphene residues found in the SPMDs is typical of "weathered" toxaphene and represents the highest concentration of an OC pesticide at all sites but Kansas City. Another residue of interest is pentachloroanisole (PCA). This contaminant likely results from past pentachlorophenol usage as a wood preservative.

Also presented in Table 1 are the results of the analysis of the SPMDs from the five deployment sites for PCB residues. While PCBs were detected in all samples, these residues were not significantly greater than the background associated with

sample processing and analysis. Consequently, it is not possible to define PCB residues in more detail than their presence at very low levels but there is no evidence of a point source.

The results of the analysis of individual samples for OCs at Sioux City, Nebraska City, Kansas City, Glasgow, and Hermann are presented respectively in Tables 2 - 6. It is readily apparent from these data that the SPMDs function in a highly reproducible manner. Statistical analysis of these data (see Tables 7-11) indicate that the coefficient of variation between samples generally ranged from 10 to 35%. The one exception is o,p'-DDE which had an average coefficient of variation of 51%. A similar analysis for the determination of toxaphene residues is presented in Table 12. As with the other OCs, the coefficient of variation between replicate analyses ranged from 10 to 35%.

We compared the precision obtained with the SPMDs to that obtained with analysis of feral fish samples. In general, it has been the experience of researchers at the NFCRC, that analysis of individual fish for organic contaminants typically result in coefficients of variations of 20 to several hundred percent as compared to 10 to 35% for SPMD's. Quite obviously, SPMDs offer a unique approach to defining the potential for exposure of aquatic organisms to contaminants and to providing a more precise and more realistic estimation than analysis of feral aquatic organisms.

An examination of the data in Tables 2 - 6 and 12 presents a limited comparison between SPMDs containing a slimicide and those without such a treatment. The SPMDs in this project were treated with a commercially available, EPA approved slimicide in an effort to reduce periphytic growth. The elimination of periphyton was deemed desirable in order to maintain a high flux rate of contaminants into the SPMDs. The slimicide treatment did not significantly reduce the growth of periphyton. The residue concentrations obtained with both treated and untreated SPMDs were essentially equivalent. Future SPMDs deployed in the field will, therefore, not be treated with slimicide. Research using dissipation rate standards will be conducted in an effort to correct for reduction in uptake rates resulting from SPMD fouling.

The results of analyses of the SPMDs from the five deployment sites for PAH residues are summarized in Tables 13 (with slimicide treatment) and 14 (without slimicide treatment). A limited number of PAHs (i.e. fluoranthene, pyrene and chrysene) were present at Nebraska City, Kansas City and Glasgow with phenanthrene being present only at the Kansas City site. The paucity of PAH residues may be due to the generally rural nature of the deployment sites (i.e. the Kansas City site was above the metropolitan area of Kansas City) or perhaps to other factors such as the extremely low water solubility of some PAHs and the high suspended sediment load or extensive metabolism by a diverse microbial

community. There is no evidence, however, of a point source discharge of PAH containing pollution near any of the five deployment sites.

The results of analysis of replicate SPMD samples for the Priority Pollutant PAHs are given in Tables 15 - 19. As with the OC results, the PAH residues are very reproducible. Moreover, because no metabolism of PAHs occurred in the SPMDs these values are realistic estimations of the exposure of aquatic organisms to PAHs in the water column.

The identities of the PAHs and the major OCs (e.g. chlordanes, dieldrin, etc.) in SPMD samples from Kansas City and Glasgow were verified by gas chromatography/mass spectrometry (GC/MS). In addition, the GC/MS analysis (see GC/MS report in the Sample Processing and Analysis Appendix) revealed the probable presence of the herbicide Prowl®. This herbicide, N-(l-ethylpropyl)-3,4-dimethyl-2,6-dinitro benzenamine, is used for pre- and post-emergence in field corn, soybeans, tobacco, etc. Other tentatively identified compounds included low levels of brominated diphenylethers, the insecticide chlorpyrifos, and the herbicide trifluralin.

The SPMDs were deployed in protected areas (i.e. behind wing dams) of the Missouri River channel in current velocities of approximately 0.5 m/s. Moreover, the flow was essentially constant during the 28 day exposure (i.e. no major

rainfall events or runoff). Consequently, the water temperature was estimated to have varied by no more than 5°C between deployment sites. Because of these stable conditions, the residues sequestered by the SPMDs at the respective sites can be directly compared without employing a temperature correction. Based upon the residues sequestered by the SPMDs, the following index results (lowest to highest); OC pesticides and toxaphene: Sioux City, Nebraska City, Kansas City, Hermann, and Glasgow; PAHs: Sioux City and Hermann, Kansas City, Nebraska City, and Glasgow. Residues of PCBs were generally in the same range at all sites and were typical of background levels.

Recognizing the unique nature of the present data, it is unfortunate that funding for the second year of this project was canceled. The research to be conducted during the second year of the project was designed to provide data concerning the presence of organic contaminants in major tributaries of the Missouri River. This data would have provided the benchmark for potential major sources of contaminants - other than atmospheric input or generalized runoff - to the main stem of the Missouri River.

VI. CONCLUSIONS

The following summarizes the major accomplishments and conclusions of this study:

- The relative ease of deployment, exposure, and recovery of SPMDs (28 day integrative sampling regimen) in a large riverine system was demonstrated.

- The ability of the SPMDs to concentrate bioavailable contaminants present in the main stem of the Missouri River was demonstrated.

- OC pesticides were the major class of bioavailable organic contaminants found at all sites in the river.

- The analysis of replicate SPMD samples demonstrated the greater reproducibility of SPMDs compared to analysis of feral fish.

- The SPMD approach provided a relative ranking of the various sites in regards to the concentration of bioavailable organic contaminants.

- SPMDs were successfully used to sequester contaminants normally metabolized by fish (PAHs) and unknowns (eg. brominated diphenyl ethers).

- The data from the SPMDs provided an assessment of habitat quality in regards to the presence of bioavailable organic contaminants.

The data presented in this report represents an estimation of the types of lipophilic organic contaminants aquatic species are exposed to in the main stem of the Missouri River. Further, this data provides an estimation of the truly bioavailable (i.e. by the respiration process) portion of these residues. As such this data set is unique and serves as a benchmark for determing the exposure of aquatic organisms to bioavailable contaminant residues under normal flow conditions in the main stem of the Missouri River.

By using the SPMD technique to sequester bioavailable contaminant residues, it is possible to ascertain the quality of aquatic habitats. This data is then available to resource managers to use in their decision making process regarding the status of fishery resources, endangered species, health of existing and potential refuges and the state of ecosystems in general. We envision an expanding role for the SPMD technology in a broad array of Fish and Wildlife Service activities.

VII. RECOMMENDATIONS FOR POST FLOOD (1993) STUDIES

A. If implemented, the flood way concept provides an opportunity to address national objectives for biodiversity and ecosystem based management. The extensive flooding resulted in alteration of vast areas of land previously used for agricultural and industrial operations. If this land becomes available for fish and wildlife habitat, particularly refuges, it is critical to

define the potential for adverse impacts, and compare the quality of these habitats with those in the main stem of the river. This could be accomplished by using SPMDs to identify contaminants in these habitats and comparing this information with other measures of habitat quality. Other measures might include a habitat-based analysis of invertebrate and/or fish productivity and community diversity.

B. Repeat the present study to determine the effect of flooding on the bioavailable contaminant loading in the main stem of the Missouri River. The flood of 1993 resulted in extensive erosion of soils contaminated with agricultural chemicals and resuspension of contaminated sediments. Consequently, the amounts of bioavailable contaminant residues may have increased dramatically in the Missouri River.

C. Determine the contribution of major tributaries to the contaminant load of the Missouri River. This project would be an expanded version of the unfunded second year of the present study. By deploying SPMDs in major tributary streams, the contribution of the tributaries to the main stem contaminant load can be defined.

D. Determine the presence of previously unrecognized contaminants. The massive redistribution of sediments and soils potentially introduced a wide

array of previously undetected contaminants into the Missouri River system. Because the SPMDs concentrate a broad spectrum of lipophilic contaminants without metabolic losses, they are ideally suited for determining the presence of unrecognized contaminants. Combined with bioassays and GC/MS analysis, the SPMDs function to provide data regarding the presence, identify and potential significance of these unknowns.

E. Determine the contribution of invertebrates to the contaminant loading of certain fish species in the Missouri River. Since most riverine fish species, including the endangered pallid sturgeon, rely primarily on invertebrates as a food source, it is critical to determine the extent that invertebrates contribute to contaminant loading in newly altered land areas that these fishes use, and compare this with the main stem of the river. This could be accomplished by directly comparing contaminant residues in SPMDs with those in filter collectors and detritivorous invertebrates collected from these habitats.

TABLE 1 ORGANOCHLORINE Residues in Missouri River SPMDs

NG / SAMPLE **SUMMARY OF RIVER SPMD SITES**

	SIOUX CITY N=3	NEBRASKA CITY N=4	KANSAS CITY N=4	GLASGOW N=4	HERMANN N=4
	NG	NG	NG	NG	NG
HCB	<4.0	<4.0	<4.0	<4.0	<4.0
PCA	2.1	21	25	41	37
ALPHA BHC	18	7.9	3	3.6	2.1
LINDANE	7.9	6.1	8.8	5.4	3.8
BETA BHC	1.6	1.6	<1.4	<1.4	<1.4
HEPTACHLOR	<1.0	5.8	5.7	5.9	3.3
DELTA BHC	<1.0	<1.0	1.7	1.6	<1.0
DACTHAL	<5.5	33	21	15	<5.5
OXYCHLORDANE	2.4	12	17	29	23
HEPTACHLR EPOX	22	92	110	160	170
T-CHLORDANE	4.9	60	89	180	150
T-NONACHLOR	4.4	34	49	110	85
C-CHLORDANE	7.4	75	100	240	190
o,p'-DDE	2.8	4.1	5.3	11	15
DIELDRIN	64	420	590	810	650
p,p'-DDE	4.4	32	39	70	45
o,p'-DDD	4.4	14	18	27	22
ENDRIN	1.2	0.7	3.2	2.4	<1.0
C-NONACHLOR	<0.5	13	16	36	28
o,p'-DDT	<5.1	<5.1	<5.1	<5.1	<5.1
p,p'-DDD	9.9	21	26	43	40
p,p'-DDT	<1.0	14	19	18	8.9
MIREX	<1.0	<1.0	<1.0	<1.0	<1.0
METHOXYCHLOR	<6.4	<6.4	<6.4	<6.4	<6.4
PCBs (Aroclor 1254)	<350	<350	<350	380	<350
Toxaphene Residue	100	430	540	880	680

NOTE: Values in table are corrected for Field Blank background for each site.
Each Sample is comprised of 2 SPMDs. Each SPMD= 1.85g Triolein. (total=3.7g)
M D L s are indicated with the " < " values.

TABLE 2 OC PESTICIDES in Missouri River SPMDs

Nanograms / Sample **SIOUX CITY**

	Sioux #a w/o slimicide	Sioux#1	Sioux #2	Sioux #3
HCB	<4.0	<4.0	<4.0	<4.0
PCA	1.6	2.7	2.2	1.3
ALPHA BHC	13.1	17.3	18.3	18.4
LINDANE	5.6	7.8	8.1	8.0
BETA BHC	0.0	< 1.0	< 1.0	< 1.0
HEPTACHLOR	< 1.0	< 1.0	< 1.0	< 1.0
DELTA BHC	< 1.0	< 1.0	< 1.0	< 1.0
DACTHAL	< 5.0	< 5.0	< 5.0	< 5.0
OXYCHLORDANE	1.6	2.4	2.4	2.3
HEPTACHLOR EPOXIDE	13.1	22.6	22.3	22.4
T-CHLORDANE	3.3	5.1	4.9	4.6
T-NONACHLOR	1.8	5.7	3.9	3.5
C-CHLORDANE	2.0	10.0	6.4	5.7
o,p'-DDE	0.9	3.7	2.1	2.7
DIELDRIN	35.5	65.1	66.4	61.4
p,p'-DDE	2.7	5.6	3.1	4.5
o,p'-DDD	2.6	4.1	4.2	3.8
ENDRIN	0.0	1.3	1.4	1.0
C-NONACHLOR	<0.5	<0.5	<0.5	<0.5
o,p'-DDT	<5.1	<5.1	<5.1	<5.1
p,p'-DDD	5.4	10.3	9.8	9.7
p,p'-DDT	< 1.0	< 1.0	< 1.0	< 1.0
MIREX	< 1.0	< 1.0	< 1.0	< 1.0
METHOXYCHLOR	< 6.4	< 6.4	< 6.4	< 6.4

Note: Values in table are corrected for Field Blank background.
Each sample = 2 SPMDs = 3.7 g total triolein.
MDLs are indicated as "<" values.

TABLE 3

OC PESTICIDE Residues in Missouri River SPMDs

Nanograms / Sample

NEBRASKA CITY

	Nebraska #a	#b	Nebraska #1	Nebraska #2	Nebraska #3	Nebraska #4
	.....w/oslimicide.....					
HCB	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
PCA	13.3	21.1	19.2	19.0	28.0	17.2
ALPHA BHC	6.3	4.2	6.1	7.8	12.0	5.8
LINDANE	3.4	6.1	4.7	6.1	8.8	4.6
BETA BHC	<1.0	5.5	<1.0	4.3	2.3	<1.0
HEPTACHLOR	3.5	6.1	7.0	6.6	2.7	6.8
DELTA BHC	0.7	1.6	<1.0	<1.0	<1.0	<1.0
DACTHAL	11.2	20.4	18.1	43.7	30.3	38.5
OXYCHLORDANE	6.6	10.7	10.1	12.1	12.9	13.0
HEPTACHLOR EPOXIDE	40.9	80.8	91.0	94.3	100.5	83.4
T-CHLORDANE	25.5	50.6	55.4	61.0	66.5	58.4
T-NONACHLOR	11.3	15.3	32.2	33.6	39.4	32.0
C-CHLORDANE	30.4	62.4	68.5	76.0	82.1	73.6
o,p'-DDE	2.2	5.5	1.6	3.4	8.4	3.1
DIELDRIN	180.4	314.9	411.1	431.1	453.6	369.1
p,p'-DDE	12.0	3.9	31.1	30.8	37.2	30.1
o,p'-DDD	6.6	14.2	10.2	15.1	17.6	13.5
ENDRIN	0.9	1.5	<0.5	0.9	1.0	0.8
C-NONACHLOR	6.7	9.0	10.4	11.9	13.6	15.9
o,p'-DDT	<5.1	<5.1	<5.1	<5.1	<5.1	<5.1
p,p'-DDD	14.4	18.5	20.6	21.9	21.4	19.2
p,p'-DDT	1.7	4.4	11.8	16.1	11.4	16.4
MIREX	<1.0	<1.0	<1.0	<1.0	<1.0	1.8
METHOXYCHLOR	<6.4	<6.4	<6.4	<6.4	<6.4	<6.4

Note: Values in table are corrected for Field Blank background.
Each sample = 2 SPMDs = 3.7g total triolein.
MDLs are indicated as " < " values.

TABLE 4 OC PESTICIDE Residues in Missouri River SPMDs

Nanograms / Sample **KANSAS CITY**

	Kansas #a	#b	Kansas #1	Kansas #2	Kansas #3	Kansas #4
	.....w/o slimicide.....					
HCB	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
PCA	14.5	22.7	25.6	23.6	30.4	21.3
ALPHA BHC	1.8	3.1	3.0	2.4	3.4	3.1
LINDANE	6.3	9.4	8.3	8.4	10.4	8.2
BETA BHC	<1.0	<1.0	<1.0	<1.0	1.9	<1.0
HEPTACHLOR	3.4	4.8	5.4	5.9	6.9	4.7
DELTA BHC	1.0	1.4	1.5	1.6	2.5	1.2
DACTHAL	15.9	20.6	18.0	18.2	27.0	20.3
OXYCHLORDANE	12.7	16.7	15.8	18.4	20.6	14.9
HEPTACLR EPOX	81.7	95.4	103.5	110.4	142.7	95.1
T-CHLORDANE	68.5	89.1	80.2	85.7	107.4	81.0
T-NONACHLOR	22.9	50.0	43.5	49.1	56.8	45.3
C-CHLORDANE	73.4	95.0	87.9	94.5	125.2	95.3
o,p'-DDE	3.7	5.2	3.7	4.2	8.7	4.3
DIELDRIN	532.6	563.4	549.7	522.2	737.1	566.8
p,p'-DDE	31.3	45.1	37.1	38.2	44.6	37.4
o,p'-DDD	13.2	17.7	15.5	18.4	21.5	17.2
ENDRIN	2.6	2.3	3.4	2.9	3.7	2.6
C-NONACHLOR	13.0	16.5	15.9	15.0	18.3	15.1
o,p'-DDT	1.6	2.9	2.8	3.7	3.4	3.2
p,p'-DDD	26.0	25.6	21.6	33.0	27.3	22.9
p,p'-DDT	10.6	17.1	22.9	23.7	16.9	11.9
MIREX	-0.7	-0.7	<1.0	<1.0	<1.0	<1.0
METHOXYCHLOR	-1.3	-1.3	<6.4	<6.4	<6.4	<6.4

Note: Values in table are corrected for field blank background.
Each Sample = 2SPMDs = 3.7g/ total triolein.
MDLs are indicated as " < " values.

TABLE 5 OC PESTICIDES in Missouri River SPMDs

Nanograms / Sample GLASGOW

	Glasgow #a	#b	Glasgow #1	Glasgow #2	Glasgow #3	Glasgow #4
	.....w/o slimicide.....					
HCB	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
PCA	43.2	29.2	51.0	38.8	42.7	28.6
ALPHA BHC	3.9	2.5	3.6	3.0	3.5	2.0
LINDANE	4.7	4.4	7.2	4.9	4.3	4.0
BETA BHC	1.6	0.0	0.5	0.7	1.6	0.0
HEPTACHLOR	7.3	5.4	7.2	5.6	6.8	4.9
DELTA BHC	1.2	3.1	2.1	2.6	1.2	3.1
DACTHAL	15.8	10.7	24.6	5.4	13.5	8.4
OXYCHLORDANE	30.3	19.9	34.7	26.1	29.8	19.4
HEPTACHLOR EPOXIDE	172.7	130.1	179.8	154.9	172.1	129.5
T-CHLORDANE	202.5	141.9	209.0	167.4	197.6	137.0
T-NONACHLOR	117.8	86.7	125.7	101.4	111.7	80.6
C-CHLORDANE	279.5	195.3	270.7	221.0	279.0	194.8
o,p'-DDE	16.7	5.8	8.3	17.2	16.7	5.8
DIELDRIN	891.5	689.1	852.8	754.6	890.7	688.2
p,p'-DDE	82.0	60.5	70.1	63.7	79.6	58.1
o,p'-DDD	28.7	20.1	31.9	28.1	28.7	20.1
ENDRIN	2.1	2.6	3.7	3.5	2.1	2.6
C-NONACHLOR	41.0	28.1	40.2	32.7	40.8	27.8
o,p'-DDT	3.7	1.4	8.9	1.2	3.5	1.2
p,p'-DDD	41.0	33.3	43.4	36.0	41.0	33.3
p,p'-DDT	18.2	17.2	21.5	16.7	16.8	15.7
MIREX	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
METHOXYCHLOR	<6.4	<6.4	<6.4	<6.4	<6.4	<6.4

Note: Values in table are corrected for the field blank background.
Each Sample = 2 SPMDs = 3.7g triolein.
MDLs are indicated as " < " values.

TABLE 6

OC PESTICIDES in Missouri River SPMDs

Nanograms / Sample

HERMANN

	Hermann #a	#b	Hermann #1	Hermann #2	Hermann #3	Hermann #4
	.....w/o slimicide.....					
HCB	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
PCA	44.4	42.0	39.6	24.6	43.8	41.4
ALPHA BHC	2.6	2.4	2.1	2.1	2.2	2.0
LINDANE	4.7	4.5	4.7	2.4	4.2	4.0
BETA BHC	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4
HEPTACHLOR	4.3	3.2	3.6	2.7	4.0	2.9
DELTA BHC	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
DACTHAL	<5.5	<5.5	<5.5	<5.5	<5.5	<5.5
OXYCHLORDANE	29.8	20.2	23.5	16.7	29.8	20.2
HEPTACHLOR EPOXIDE	197.4	172.6	193.2	144.0	196.8	172.1
T-CHLORDANE	179.4	133.1	164.9	117.1	178.6	132.4
T-NONACHLOR	104.8	73.6	95.9	74.9	100.6	69.5
C-CHLORDANE	224.6	165.5	211.0	162.7	213.4	154.3
o,p'-DDE	13.9	5.3	12.1	27.9	13.6	5.0
DIELDRIN	902.4	709.0	569.6	440.5	901.6	708.3
p,p'-DDE	51.8	44.0	53.2	37.6	48.1	40.3
o,p'-DDD	26.7	20.0	27.3	15.3	26.5	19.8
ENDRIN	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
C-NONACHLOR	33.4	25.7	32.4	21.1	33.4	25.6
o,p'-DDT	<5.1	<5.1	<5.1	<5.1	<5.1	<5.1
p,p'-DDD	47.6	37.6	44.7	29.5	47.6	37.6
p,p'-DDT	12.5	8.7	10.7	4.9	11.8	8.0
MIREX	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
METHOXYCHLOR	<6.4	<6.4	<6.4	<6.4	<6.4	<6.4

Note: Values in table are corrected for field blank background.
Each sample = 2 SPMDs = 3.7g triolein
MDLs are indicated a " < " values.

TABLE 7 OC PESTICIDES in Missouri River SPMDs

Nanograms/ Sample **SIOUX CITY**

	Average N=3	Coef. Var. %	Range
HCB	<4.0	–	–
PCA	2.1	35	1.3–2.7
ALPHA BHC	18.0	3	17–18
LINDANE	7.9	2	7.8–8.1
BETA BHC	< 1.0	–	–
HEPTACHLOR	< 1.0	–	–
DELTA BHC	< 1.0	–	–
DACTHAL	< 5.0	–	–
OXYCHLORDANE	2.4	3	2.3–2.4
HEPTACHLOR EPOXIDE	22.4	1	22.3–22.6
T–CHLORDANE	4.9	5	4.6–5.1
T–NONACHLOR	4.4	27	3.5–5.7
C–CHLORDANE	7.4	32	5.7–10.
o,p'–DDE	2.8	28	2.1–3.7
DIELDRIN	64.3	4	61.4–66.4
p,p'–DDE	4.4	29	3.1–5.6
o,p'–DDD	4.0	6	3.8–4.1
ENDRIN	1.2	17	1.0–1.4
C–NONACHLOR	<0.5	–	–
o,p'–DDT	<5.1	–	–
p,p'–DDD	9.9	3	9.7–10.3
p,p'–DDT	< 1.0	–	–
MIREX	< 1.0	–	–
METHOXYCHLOR	< 6.4	–	–

Note: Values in table are corrected for Field Blank background.
Each sample = 2 SPMDs = 3.7 g total triolein.
MDLs are indicated as "<" values.

TABLE 8 OC PESTICIDE Residues in Missouri River SPMDs

Nanograms / Sample **NEBRASKA CITY**

	Average N=3	Coef. Var. %	Range
HCB	<4.0	–	–
PCA	20.9	23	17–18
ALPHA BHC	7.9	36	5.8–12.
LINDANE	6.1	32	4.6–8.8
BETA BHC	1.6	–	<1.0–4.3
HEPTACHLOR	5.8	36	2.7–7.0
DELTA BHC	<1.0	–	<1.0
DACTHAL	32.7	34	18–44
OXYCHLORDANE	12.0	11	10–13
HEPTACHLOR EPOXIDE	92.3	8	83–100
T–CHLORDANE	60.3	8	55–66
T–NONACHLOR	34.3	10	32–39
C–CHLORDANE	75.1	8	69–82
o,p'–DDE	4.1	72	1.6–8.4
DIELDRIN	416.2	9	370–450
p,p'–DDE	32.3	10	30–37
o,p'–DDD	14.1	22	10–17
ENDRIN	0.7	67	<0.5–1.0
C–NONACHLOR	13.0	18	10–16
o,p'–DDT	<5.1	–	–
p,p'–DDD	20.8	6	19–21
p,p'–DDT	13.9	19	11–16
MIREX	<1.0	–	<1.0–1.8
METHOXYCHLOR	<6.4	–	–

Note: Values in table are corrected for Field Blank background.
Each sample = 2 SPMDs = 3.7g total triolein.
MDLs are indicated as " < " values.

TABLE 9 OC PESTICIDE Residues in Missouri River SPMDs

Nanograms / Sample **KANSAS CITY**

	Average N = 4	Coef.Var. (%)	Range
HCB	<4.0	–	–
PCA	25.2	15	21–30
ALPHA BHC	3.0	15	2.4–3.4
LINDANE	8.8	12	8.2–10.4
BETA BHC	<1.0	–	<1.0–1.9
HEPTACHLOR	5.7	17	4.7–6.9
DELTA BHC	1.7	32	1.2–2.5
DACTHAL	20.9	20	18–27
OXYCHLORDANE	17.4	15	15–21
HEPTACLR EPOX	112.9	18	95–143
T–CHLORDANE	88.6	14	80–107
T–NONACHLOR	48.7	12	43–57
C–CHLORDANE	100.7	17	87–125
o,p'–DDE	5.3	44	3.7–8.7
DIELDRIN	593.9	16	550–740
p,p'–DDE	39.3	9	37–45
o,p'–DDD	18.2	14	16–21
ENDRIN	3.2	16	2.6–3.7
C–NONACHLOR	16.1	10	16–18
o,p'–DDT	<5.1	–	2.8–3.7
p,p'–DDD	26.2	20	22–33
p,p'–DDT	18.9	29	12–24
MIREX	<1.0	–	–
METHOXYCHLOR	<6.4	–	–

Note: Values in table are corrected for field blank background.
Each Sample = 2SPMDs = 3.7g/ total triolein.
MDLs are indicated as " < " values.

TABLE 10 OC PESTICIDES in Missouri River SPMDs

Nanograms/Sample **GLASGOW**

	Average N=4	Coef.Var. (%)	Range
HCB	<4.0	–	–
PCA	40.3	23	29–51
ALPHA BHC	3.0	24	2.0–3.6
LINDANE	5.1	28	4.0–7.2
BETA BHC	0.7	98	<1.0–1.6
HEPTACHLOR	6.1	18	4.9–7.2
DELTA BHC	2.2	35	1.2–3.1
DACTHAL	13.0	65	5.4–25
OXYCHLORDANE	27.5	23	19–35
HEPTACHLOR EPOXIDE	159.1	14	130–180
T–CHLORDANE	177.7	18	140–210
T–NONACHLOR	104.9	18	81–125
C–CHLORDANE	241.4	17	195–280
o,p'–DDE	12.0	48	5.8–17
DIELDRIN	796.5	12	755–890
p,p'–DDE	67.9	14	58–80
o,p'–DDD	27.2	18	20–32
ENDRIN	3.0	26	2.1–3.7
C–NONACHLOR	35.4	18	28–41
o,p'–DDT	<5.1	–	–
p,p'–DDD	38.4	12	33–43
p,p'–DDT	17.7	15	16–22
MIREX	<1.0	–	–
METHOXYCHLOR	<6.4	–	–

Note: Values in table are corrected for the field blank background.
Each Sample = 2 SPMDs = 3.7g triolein.
MDLs are indicated as " < " values.

TABLE 11 OC PESTICIDES in Missouri River SPMDs

Nanograms / Sample **HERMANN**

	Average N=4	Coef.Var. (%)	Range
HCB	<4.0	–	–
PCA	37.4	23	25–44
ALPHA BHC	2.1	4	2.0–2.2
LINDANE	3.8	26	2.4–4.7
BETA BHC	<1.4	–	–
HEPTACHLOR	3.3	18	2.7–4.0
DELTA BHC	<1.0	–	–
DACTHAL	<5.5	–	–
OXYCHLORDANE	22.5	25	17–30
HEPTACHLOR EPOXIDE	176.5	14	140–190
T–CHLORDANE	148.2	19	120–180
T–NONACHLOR	85.2	18	70–100
C–CHLORDANE	185.4	17	150–210
o,p'–DDE	14.6	66	5.0–28
DIELDRIN	655.0	30	440–710
p,p'–DDE	44.8	16	38–53
o,p'–DDD	22.2	26	15–27
ENDRIN	<1.0	–	–
C–NONACHLOR	28.1	21	21–33
o,p'–DDT	<5.1	–	<1.0–2.3
p,p'–DDD	39.8	20	30–45
p,p'–DDT	8.9	35	4.9–12
MIREX	<1.0	–	–
METHOXYCHLOR	<6.4	–	–

Note: Values in table are corrected for field blank background.
Each sample = 2 SPMDs = 3.7g triolein
MDLs are indicated a " < " values.

TABLE 12 TOXAPHENE Residues in Missouri River SPMDs

SAMPLE	TOTAL TOXAPHENE – NG / SAMPLE				
	SIOUX	NEBRASKA	KANSAS	GLASGOW	HERMANN
w/o slimicide #a	130	260	630	920	970
w/o slimicide #b		460	700	1070	770
#1	160	540	450	870	980
#2	150	560	550	1100	550
#3	170	450	720	960	870
#4		420	690	820	570
Average (corrected)	100	433	543	878	683
Coef. Var. (%)	10	14	25	13	33
RANGE	90–110	360–500	390–660	760–1040	490–920
Total Toxaphene	**100**	**430**	**540**	**880**	**680**

TABLE 13 PAH Residues in Missouri River SPMDs

UG / SAMPLE **SUMMARY OF RIVER SPMD SITES**

Priority Pollutant PAHs	Sioux City N=3	Nebraska City N=4	Kansas City N=4	Glasgow N=4	Hermann N=4
naphthalene	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthalene	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthene	<0.10	<0.10	<0.10	<0.10	<0.10
fluorene	<0.10	<0.10	<0.10	<0.10	<0.10
phenanthrene	<0.10	<0.10	**0.18**	<0.10	<0.10
anthracene	<0.10	<0.10	<0.10	<0.10	<0.10
fluoranthene	<0.10	**0.86**	**0.73**	**1.09**	<0.10
pyrene	<0.10	**0.85**	**0.73**	**1.24**	<0.10
benz(a)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10
chrysene	<0.10	**0.16**	**0.18**	**0.31**	<0.10
benzo(b)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(k)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(a)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10
indeno(123cd)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10
dibenz(ah)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(ghi)perylene	<0.10	<0.10	<0.10	<0.10	<0.10

Note: 2 SPMDs per Sample
Values in table are corrected for field blank background for each site.
Each sample is comprised of 2 SPMDs. Each SPMD= 1.85 g triolein. (total=3.7g)
M D L s are indicated with the " < " values.

TABLE 14 PAH Residues in Missouri River SPMDs

UG / SAMPLE ***WITHOUT SLIMICIDE***

Priority Pollutant PAHs	Sioux City N=1	Nebraska City N=2	Kansas City N=2	Glasgow N=2	Hermann N=2
naphthalene	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthalene	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthene	<0.10	<0.10	<0.10	<0.10	<0.10
fluorene	<0.10	<0.10	<0.10	<0.10	<0.10
phenanthrene	<0.10	<0.10	**0.16**	<0.10	<0.10
anthracene	<0.10	<0.10	<0.10	<0.10	<0.10
fluoranthene	<0.10	**0.68**	**0.69**	**1.11**	<0.10
pyrene	<0.10	**0.67**	**0.69**	**1.28**	<0.10
benz(a)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10
chrysene	<0.10	**0.10**	<0.10	**0.28**	<0.10
benzo(b)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(k)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(a)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10
indeno(123cd)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10
dibenz(ah)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(ghi)perylene	<0.10	<0.10	<0.10	<0.10	<0.10

Note: 2 SPMDs per Sample
Values in table are corrected for field blank background for each site.
Each sample is comprised of 2 SPMDs. Each SPMD= 1.85 g triolein. (total=3.7g)
M D L s are indicated with the " < " values.

TABLE 15 PAH Residues in Missouri River SPMDs

UG / Sample **SIOUX CITY**

Priority Pollutant PAHs	Sioux #a w/o slimicide	Sioux #1	Sioux #2	Sioux #3
naphthalene	<0.10	<0.10	<0.10	<0.10
acenaphthalene	<0.10	<0.10	<0.10	<0.10
acenaphthene	<0.10	<0.10	<0.10	<0.10
fluorene	<0.10	<0.10	<0.10	<0.10
phenanthrene	<0.10	<0.10	<0.10	<0.10
anthracene	<0.10	<0.10	<0.10	<0.10
fluoranthene	<0.10	<0.10	<0.10	<0.10
pyrene	<0.10	<0.10	<0.10	<0.10
benz(a)anthracene	<0.10	<0.10	<0.10	<0.10
chrysene	<0.10	<0.10	<0.10	<0.10
benzo(b)fluoranthene	<0.10	<0.10	<0.10	<0.10
benzo(k)fluoranthene	<0.10	<0.10	<0.10	<0.10
benzo(a)pyrene	<0.10	<0.10	<0.10	<0.10
indeno(123cd)pyrene	<0.10	<0.10	<0.10	<0.10
dibenz(ah)anthracene	<0.10	<0.10	<0.10	<0.10
benzo(ghi)perylene	<0.10	<0.10	<0.10	<0.10

Note: 2 SPMDs per Sample
Values in table are corrected for field blank background for each site.
Each sample is comprised of 2 SPMDs. 1 SPMD= 1.85 g triolein. (total=3.7g)
M D L s are indicated with the " < " values.

TABLE 16 PAH Residues in Missouri River SPMDs

UG / Sample **NEBRASKA CITY**

Priority Pollutant PAHs	Nebraska #a	#b	Nebraska #1	Nebraska #2	Nebraska #3	Nebraska #4
	.....w/o slimicide.....					
naphthalene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthalene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
fluorene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenanthrene	<0.10	**0.13**	**0.13**	**0.14**	**0.11**	**0.11**
anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
fluoranthene	**0.41**	**0.94**	**0.89**	**0.93**	**0.82**	**0.80**
pyrene	**0.43**	**0.91**	**0.86**	**0.93**	**0.80**	**0.81**
benz(a)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
chrysene	<0.10	**0.20**	**0.14**	**0.14**	**0.18**	**0.16**
benzo(b)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(k)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(a)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
indeno(123cd)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
dibenz(ah)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(ghi)perylene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

Note: 2 SPMDs per Sample
Values in table are corrected for field blank background for each site.
Each sample is comprised of 2 SPMDs. Each SPMD= 1.85 g triolein. (total=3.7g)
M D L s are indicated with the " < " values.

TABLE 17

PAH Residues in Missouri River SPMDs

UG / Sample **KANSAS CITY**

Priority Pollutant PAHs	Kansas #a	#b	Kansas #1	Kansas #2	Kansas #3	Kansas #4
	.....w/o slimicide.....					
naphthalene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthalene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
fluorene	<0.10	<0.10	<0.10	0.11	<0.10	<0.10
phenanthrene	0.15	0.16	0.20	0.19	0.16	0.16
anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
fluoranthene	0.62	0.75	0.80	0.78	0.67	0.67
pyrene	0.64	0.74	0.80	0.78	0.67	0.67
benz(a)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
chrysene	<0.10	<0.10	0.20	0.20	0.15	0.15
benzo(b)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(k)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(a)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
indeno(123cd)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
dibenz(ah)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(ghi)perylene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

Note: 2 SPMDs per Sample
Values in table are corrected for field blank background for each site.
Each sample is comprised of 2 SPMDs. Each SPMD= 1.85 g triolein. (total=3.7g)
M D L s are indicated with the " < " values.

TABLE 18 PAH Residues in Missouri River SPMDs

UG / Sample **GLASGOW**

Priority Pollutant PAHs	Glasgow #a	#b	Glasgow #1	Glasgow #2	Glasgow #3	Glasgow #4
	.....w/o slimicide.....					
naphthalene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthalene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
fluorene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenanthrene	<0.10	<0.10	<0.10	<0.10	0.12	0.12
anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
fluoranthene	**0.97**	**1.25**	**1.25**	**0.88**	**1.25**	**0.96**
pyrene	**1.14**	**1.42**	**1.45**	**1.04**	**1.38**	**1.10**
benz(a)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
chrysene	**0.24**	**0.32**	**0.32**	**0.21**	**0.47**	**0.23**
benzo(b)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(k)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(a)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
indeno(123cd)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
dibenz(ah)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(ghi)perylene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

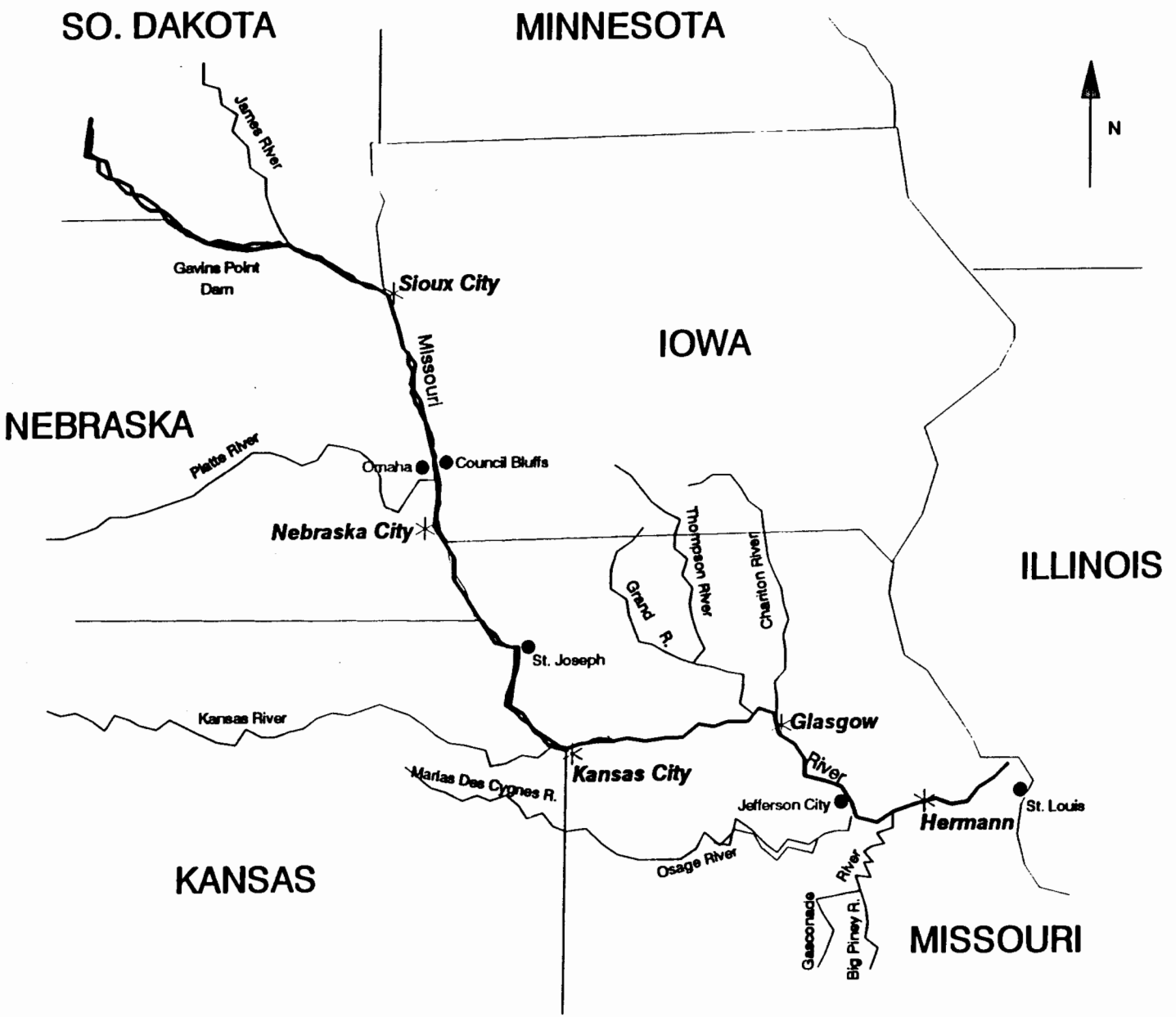
Note: 2 SPMDs per Sample
Values in table are corrected for field blank background for each site.
Each sample is comprised of 2 SPMDs. Each SPMD= 1.85 g triolein. (total=3.7g)
M D L s are indicated with the " < " values.

TABLE 19 PAH Residues in Missouri River SPMDs

UG / Sample **HERMANN**

Priority Pollutant PAHs	Hermann #a	#b	Hermann #1	Hermann #2	Hermann #3	Hermann #4
	.....w/o slimicide....					
naphthalene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthalene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
acenaphthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
fluorene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenanthrene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
pyrene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benz(a)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
chrysene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(b)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(k)fluoranthene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(a)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
indeno(123cd)pyrene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
dibenz(ah)anthracene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
benzo(ghi)perylene	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

Note: 2 SPMDs per Sample
Values in table are corrected for field blank background for each site.
Each sample is comprised of 2 SPMDs. Each SPMD= 1.85 g triolein. (total=3.7g)
M D L s are indicated with the " < " values.


SO. DAKOTA
MINNESOTA
N
James River
Gavins Point Dam
Sioux City
Missouri
IOWA
NEBRASKA
Platte River
Omaha
Council Bluffs
Nebraska City
Thompson River
Grand R.
Charlton River
ILLINOIS
St. Joseph
Kansas River
Glasgow
River
Kansas City
Marias Des Cygnes R.
Jefferson City
Hermann
St. Louis
Osage River
River
Gasconade
Big Piney R.
KANSAS
MISSOURI

Date prepared: 7/28/92

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Date revised:

DEPLOYMENT AND MAINTENANCE OF SEMIPERMEABLE PASSIVE MEMBRANE DEVICES (SPMDS) ARRANGED IN STAINLESS STEEL WIRE CAGES

The semipermeable passive membrane device (SPMD) is intended to accumulate trace concentrations of nonpolar organic chemicals (PCBs, dioxins, PAHs, organochlorine pesticides, etc.) from water (Huckins et al. 1990). The SPMD consists of a length of 2.54 cm wide layflat tubing containing a thin film of lipid (1.15 g lipid per meter of tubing). For deployment in the wire cages, the SPMDs need to be 152.4 cm long and contain 2 g of lipid. The lipid is usually triolein, but may vary from study to study. Fabrication of SPMDs is described in NFCRC SOP B5.217. Bags are to be stored refrigerated in solvent-cleaned paint cans which have been air evacuated using argon gas. For ease of sampling, the cans should be pre-labeled accordingly (i.e., site, date, device #, etc.).

A device capable of suspending 8 SPMDs vertically in the water column has been developed at NFCRC. The device consists of 304 grade stainless steel wire cloth (# 2 mesh) constructed in a 25.4 cm by 25.4 cm by 1 m rectangular wire cage mended by uncoated, soft tempered stainless steel wire (16 gauge). Two pieces of 1/2" polyethylene (25.4 cm^2) are fitted to the open ends using the same wire. For rigidity, one 3/8" X 40" piece of threaded rod is fitted and secured lengthwise through the cage along with three smaller cross-pieces (1/4" X 10") near the center of the device. Four, six inch diameter round PVC floats are mounted to the top of the unit for floatation and should not exceed a buoyancy force greater than the weight of the anchor. Anchor or anchors should be suspended on rope from an eye bolt which is coupled to the base of the 3/8" threaded rod. The length of rope should dictate approximate depth of sampler. The device will also be anchored from a 3/4" steel reinforcing rod (rebar), which is driven into the sediment, to a stainless steel cable (mounted lengthwise on the sampler) using 1/2" polyrope. The rebar is modified to hold a Ryan TempMentor (Fig.1).

The SPMDs are placed lengthwise within the cage and encircle stainless steel holding pins sheathed with nylon pressure tubing. The pins (16/sampler) consist of 4" X 3/16" bolts mounted horizontally (8 top and 8 bottom) to the wire cloth using 1" X 1/16" (#10) fender washers and 3/16" nuts. SPMDs are prevented from moving on the pins by using fender washers, wing nuts, and the nylon pressure tubing (Fig.2). The pins may be adjusted by moving the top or bottom bolts up or down a mesh to allow for the variability of bag length. SPMDs can be serviced via two trap

doors on the posterior side of the device. All SPMDs (8 max.) from a device constitutes one sample.

The devices can be suspended at any depth depending on the length of the anchor rope. However, it is preferable that the top of the sampler be at least 1-2 m below the surface of the water to allow for water fluctuation and boat traffic. The apparatus may be retrieved by grappling for the sampler line, which is connected to the rebar, or by retrieving a visibly marked locator rope, which is attached from the anchor to the bank. Autotrophic and heterotrophic organisms can be controlled by periodically dipping the devices into a biocide, directly incorporating the biocide into the lipid material within the SPMDs, or by physical removal/cleaning at periodic intervals. Blanks (i.e., SPMDs that have been subjected to all procedures but not deployed in the water) are an integral part of SPMD sampling, as is temperature monitoring. Ambient water temperature during the sampling period may be monitored electronically, gravimetrically, or both.

Deployment of SPMDs:

SPMDs are delivered to the site of deployment in solvent rinsed, air evacuated and sealed paint cans. They are placed on the holding pins within the cage immediately prior to deployment (i.e. usually aboard a research vessel), and are deployed in the following manner:

(1) Using a loop knot, tie 1/2" polyrope (length Optional) to a special clamp which is mounted to the 3/4" rebar.

(2) Activate Ryan TempMentor (if used) by plugging in the sensor, place in PVC case, and attach to a special ring which is hanging from the rebar. Record the time.

(3) Drive rebar into the sediment using a modified pole fitted with a PVC sleeve. Make sure to hold on to the rope while setting the rebar. Reel out desired length of rope and tie off to boat.

(4) Remove the lid from a blank SPMD can with a can-opener or screw-driver. Expose the blanks to the air and place where nothing will spill on them (Note: make sure the boat engine is turned off to avoid exhaust from the motor).

(5) Open the two doors on the back of the device and disassemble the eight wing nuts and corresponding washers from the top eight holding pins.

(6) Remove cans containing test SPMDs (8) from the cooler, open, and place SPMDs one at a time on the holding pins. Immediately re-cap the cans for later use, and return them to the cooler. (Note: use gloves when handling SPMDs).

(7) Reassemble the washers and wing nuts on the top holding pins, and close the doors (latch with twist ties).

(8) Assemble anchor to the bottom of sampler, and attach a locator rope to the anchor.

(9) Attach polyrope from rebar to the sampler and gently submerge the entire device while keeping the locator rope slack.

(10) Trail locator rope to the bank and mark with flags. Make sure the rope is retrievable at various depths. Lead weights can be attached to assure the rope remains on the bottom.

(11) Repeat procedure for other devices at the site.

(12) After the device(s) have been deployed, cap the blank SPMD can tightly, return it to the cooler, and record the time.

(13) Upon returning to the laboratory, transfer the blanks to a refrigerator ($\leq$4 C).

Servicing Devices and sampling SPMDs

Servicing devices is optional and may be done similar to rack and panel cleaning (see NFCRC SOPF4.1).

(1) Look for markers on the bank, retrieve the locator rope, and pull up the sampler. If unable to find rope, it may be necessary to drag for the lead line or locator rope with a large, three-pronged grappling hook. Once a line has been located, shut off boat motor.

(2) Bring the device aboard the research vessel and disassemble from the lead line. Tie off lead line to boat, and remove anchor from the device.

(3) If SPMDs are to be sampled, expose blanks, as described in (4) above (be sure and note time).

(3) Clip twist ties from the doors and begin removing the SPMDs. Bags can be removed by disassembling the top series of wingnuts and fender washers and slipping the bag off the holding pins (Note: be careful not to damage the bags when handling).

(4) Place SPMDs into the prelabeled can(s) from which they originally came. Cap and return to the cooler immediately. Reassemble the proper hardware.

(5) Remove the 3/4 inch rebar from the substrate (may need a boat-mounted winch, if available).

(6) Remove Ryan TempMentor from rebar, note the time, and unplug sensor.

(7) When all devices have been sampled at a site, seal the blanks (if any) in their respected paint can(s) and return to the cooler. Note the time.

(8) Upon returning to the laboratory, transfer the SPMDs to a refrigerator (<4 C).

References:

Huckins, J.N., M.W. Tubergen, and G.K. Manuweera. 1990. Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioaccumulation potential. Chemosphere 20:533-552.

Ryan Instruments, Inc. 1985. Operators manual and programs for the TempMentor thermograph. Kirtland, WA.

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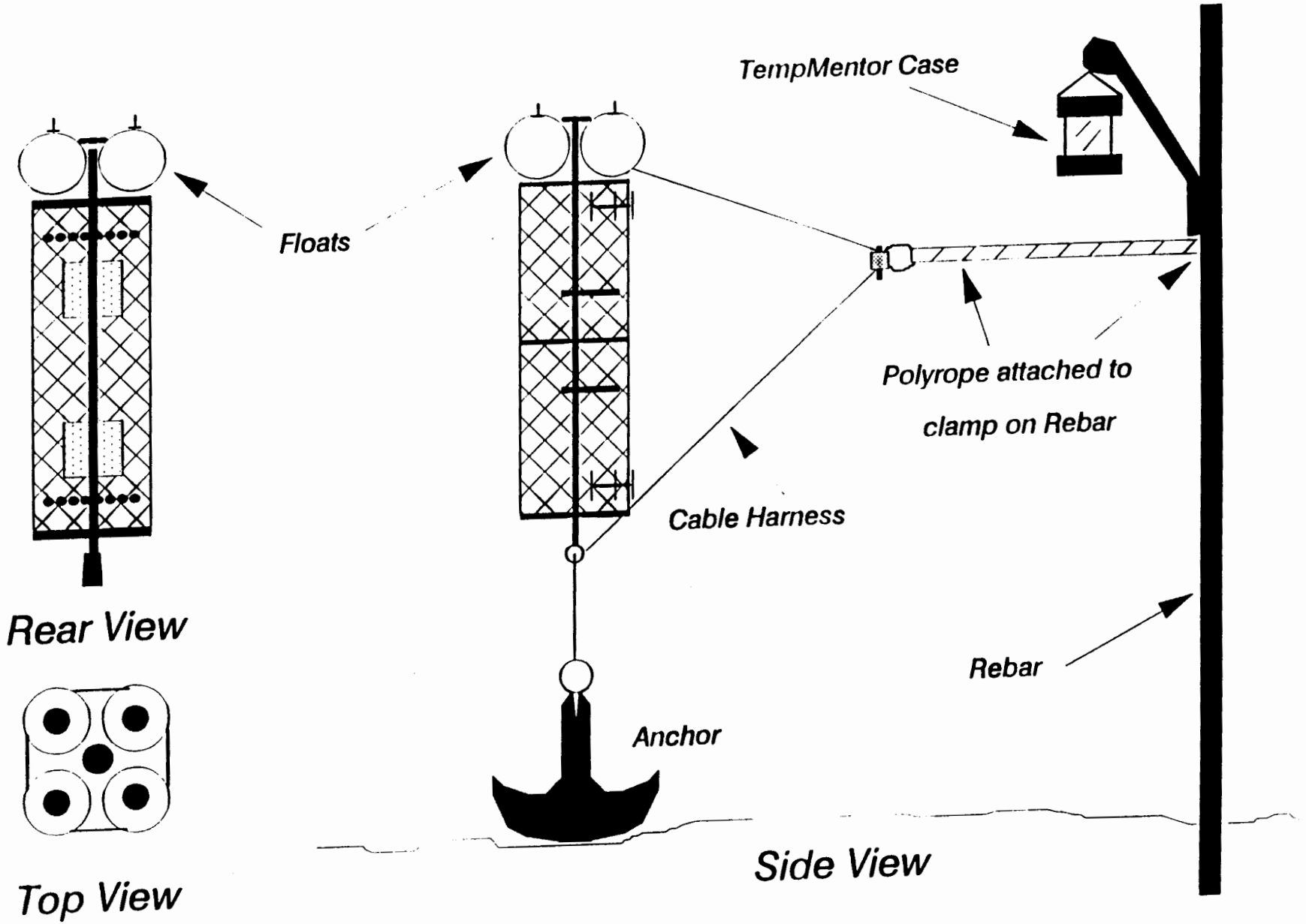

Figure 1. Vertical Deployment Configuration for SPMD's

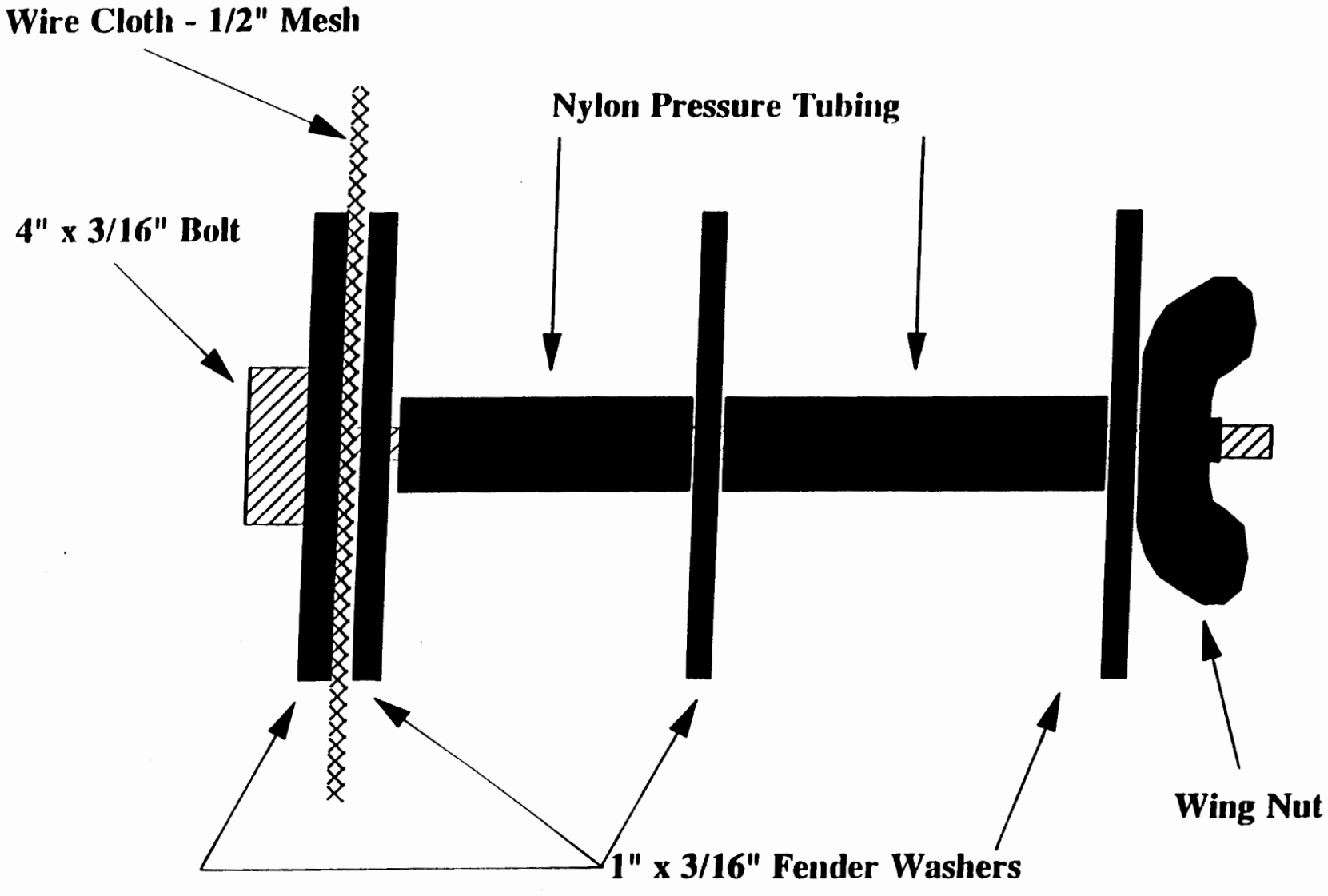

Figure 2. Side View - Parts Diagram of Stainless Steel Holding Pin for SPMD's

radiolabeled compound is spiked as described above. The radiolabeled compound is dispersed throughout the SPMD length by smoothing or rubbing the tubing with the palm of the hand. The excess air is removed and the end is resealed with three (3) heat seals. The spiked sample is dialyzed and carried through all steps (counting aliquots) as described above.

4. Field or Trip blank - These are SPMDs that were sent to the field but never removed from their shipping container. The containers were opened on site, resealed and sent back along with exposed samples. Clean these samples as descibed in Part III and carry them through the cleanup procedure as a field sample.

5. The results of all quality control samples are reviewed prior to further sample processing.

IV. **Sample fractionation** - Following the completion of the procedure(s) presented above, the sample may be processed further for target analytes using the appropriate class specific enrichment procedures.

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Date Prepared: 09/14/93

Date Revised:

Statement: For users other than NFCRC staff, this document is for reference only. It is not a citable document.

Determination of PAHs by Gas Chromatography with Photoionization Detection (GC-PID)

I. INTRODUCTION

Sample extracts that are free of interfering co-extractants are analyzed for polyaromatic hydrocarbons (PAHs) by gas chromatography with photoionization detection (GC-PID). The origin of the sample may vary: Dialysates of SPMDs, extracts of sediments, sludges, tars, etc. Clean-up choices prior to GC analysis will vary accordingly and will be only briefly addressed in this document.

II. Preliminary Clean-up and Preparation of Extracts

Although the PID at 9.5eV is specific for PAHs, certain compounds that may degrade the chromatography or be PID active should be removed prior to GC analysis. Dialysates/extracts are amenable to lipid removal by GPC (SOP#C5.155, SOP#C5.173), active copper treatment to remove elemental sulfur (SOP#C5.70), column clean-up using Florisil, potassium silicate and argentation chromatography. Size-exclusion chromatography may be performed using high performance automated GPC or gravity-flow GPC.

The cleaned extracts are carefully reduced to the appropriate final volume with rotary evaporation and under a stream of nitrogen. Since the volatility of certain PAHs (e.g. naphthalene, acenaphthene) is quite high, solvent reduction should be carried out with due care. The final solvent should be of low volatility and should not enhance GC peak tailing: Isooctane is a good choice for final solvent; hexane is also acceptable. Poorer choices are nonane, toluene, acetone, and methanol since they tend to cause tailing or shifting retention times.

Addition of Internal Standard

Azulene is incorporated at the same level in all extracts and standards. Typically this internal standard concentration is near the middle of the PAH calibration curve, i.e. 1-4μg/mL. If quantitation is based on the azulene response, and not directly on final volume, it is important that azulene is added to the entire extract at the final volume.

III. Gas Chromatographic Conditions

GC:	Hewlett Packard 5890, 7673 autoinjector.
Detector:	PID, ionization energy set to 9.5 eV, temperature=270 C.
Column:	30m x 0.25mm i.d. x 0.2u f.t. DB5 or equivalent fused silica capillary: (5% diphenyl, 94% dimethyl, 1% vinyl polysiloxane.) Retention Gap: 1m x 0.53mm i.d. deactivated.
Program:	60C, 0min, 10C/min, 100C, 3C/min, 285C, 1min.
Inj.Vol.:	1μL to 5μL
Carrier:	Hydrogen, 12psi head pressure.

GC performance is evaluated using a mixture of PAHs which contains naphthalene, pyrene, benzo[b]- and [k] fluoranthene. Under optimum conditions, the resolution (R) of B[b]- and B[k] fluoranthene should be $R_s > 0.90$, and naphthalene peak tailing factor TF should be < 1.6.

V. Calibration Standard Compositions

A five point calibration curve, with azulene as internal standard is generated. Instrument detection limits are typically 0.1 ng/μL and 0.025 ng/μL for 1μL and 5μL injections, respectively. Therefore, a working curve of 0.50 to 2.0 ng/μL or from 0.2 ng/μL to 8ng/μL can be used for 2μL and 5μL injections, respectively. At these PAH levels the 5μL injection does not cause significant peak broadening.

Standard solutions are obtained from a reliable chromatography supplier such as Supelco, Bellefonte PA or J&W Scientific, Folsom CA.

A. The following is a list of suggested calibration levels.

Level	5μL injection	1 or 2μL injection
	1μg/mL azulene	4μg/mL azulene
1	0.05 ng/μL	0.2 ng/μL
2	0.10 ng/μL	0.5 ng/μL
3	0.50 ng/μL	2.0 ng/μL
4	1.00 ng/μL	4.0 ng/μL
5	2.00 ng/μL	8.0 ng/μL

B. The following is a list of the Priority Pollutant PAH compounds quantified in this SOP. The listing is in order of elution on the 30m DB5 described above.

Compound	Ret.Time (min)
naphthalene	5.8
int.std. azulene	*8.4*
acenaphthylene	12.3
acenaphthene	13.4
fluorene	16.6
phenanthrene	23.2
anthracene	23.5
fluoranthene	32.2
pyrene	33.7
benz[a]anthracene	43.4
chrysene	43.7
benzo[b]fluoranthene	51.4
benzo[k]fluoranthene	51.6
benzo[a]pyrene	53.4
indeno[1,2,3-cd]pyrene	60.4
dibenz[a,h]anthracene	60.8
benzo[g,h,i]perylene	61.8

All stock solutions and dilutions are prepared in isooctane and stored in amber glass containers. Avoid placing solutions in intense light such as direct outdoor light.

VI Reporting of Chromatographic Results

The Nelson Analytical Chromatographic Software is used to quantitate the PAHs by internal standard method using peak areas. Attention is paid to proper baseline positioning and peak splitting. Quantitiation results are translated to Lotus files and calculations are performed in the Lotus spreadsheet format.

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roundbottom flasks.

VIII. **QA/QC** - To verify the integrity of the method and sample handling, the following blanks, spikes and controls are carried through with each set of samples. A "set" of samples consists of 1 process blank, 1 SPMD control, 1 laboratory recovery spike, a field blank (where applicable, described below) and as many samples as can be reasonably done at one time through all the procedures (generally, a maximum of 10 actual samples).

1. Process blank - This is a solvent/glassware blank. 250 mL hexane is poured into a dialysis jar and carried through all steps as a sample.

2. SPMD control - These are to be freshly prepared SPMDs. The number of SPMDs/sample and length should be the same as a field sample. They should be made according to NFCRC SOP B5.217, "Preparation of Semipermeable Membrane Devices with Model Lipid for Monitoring Organic Contaminants in Water". They are cleaned as described in Part III, dialyzed with the appropriate amount of hexane, and carried through all steps as a sample.

3. Laboratory Recovery Spike - The spike is made by preparing a fresh SPMD as descibed in 2 above except the SPMD is spiked with a radiolabeled model or the appropriate mixture of stable-labeled compounds before the heat seals are made. A radiolabeled compound that is representative of the expected contaminants in the samples is used for a spike. About 30,000 to 50,000 dpms of radioactivity are desirable for the step. During spiking, count an equal amount of the selected radiolabeled compound using 10 mL of counting cocktail in a liquid scintillation counter to verify the amount that was delivered into the SPMD. Then dialyze the recovery spike with the proper amount of hexane. Before transferring the dialysate to a round bottom flask, measure and count two 5-mL aliquots. Reduce the remaining dialysate by rotoevaporation and carry through all steps described for a sample. Count aliquots of the spike at each step to track possible losses or procedural problems.

Note: After removing the SPMD from the dialysis jar, rinse the contents of the SPMD into a graduated cylinder, record volume and count two 5-mL aliquots. Cut the SPMD membrane into small pieces and place the pieces in a counting vial, add organic solvent-based (eg. toluene) cocktail and analyze by liquid scintillation.

If there are extra field deployed SPMDs, they can be used for the spike. After the cleaning procedure described in Part III, one end of a membrane is opened and the

MISSOURI RIVER SPMDs- SAMPLE DESCRIPTION AND NAMES

Environmental Chemistry Group- USDI NFCRC

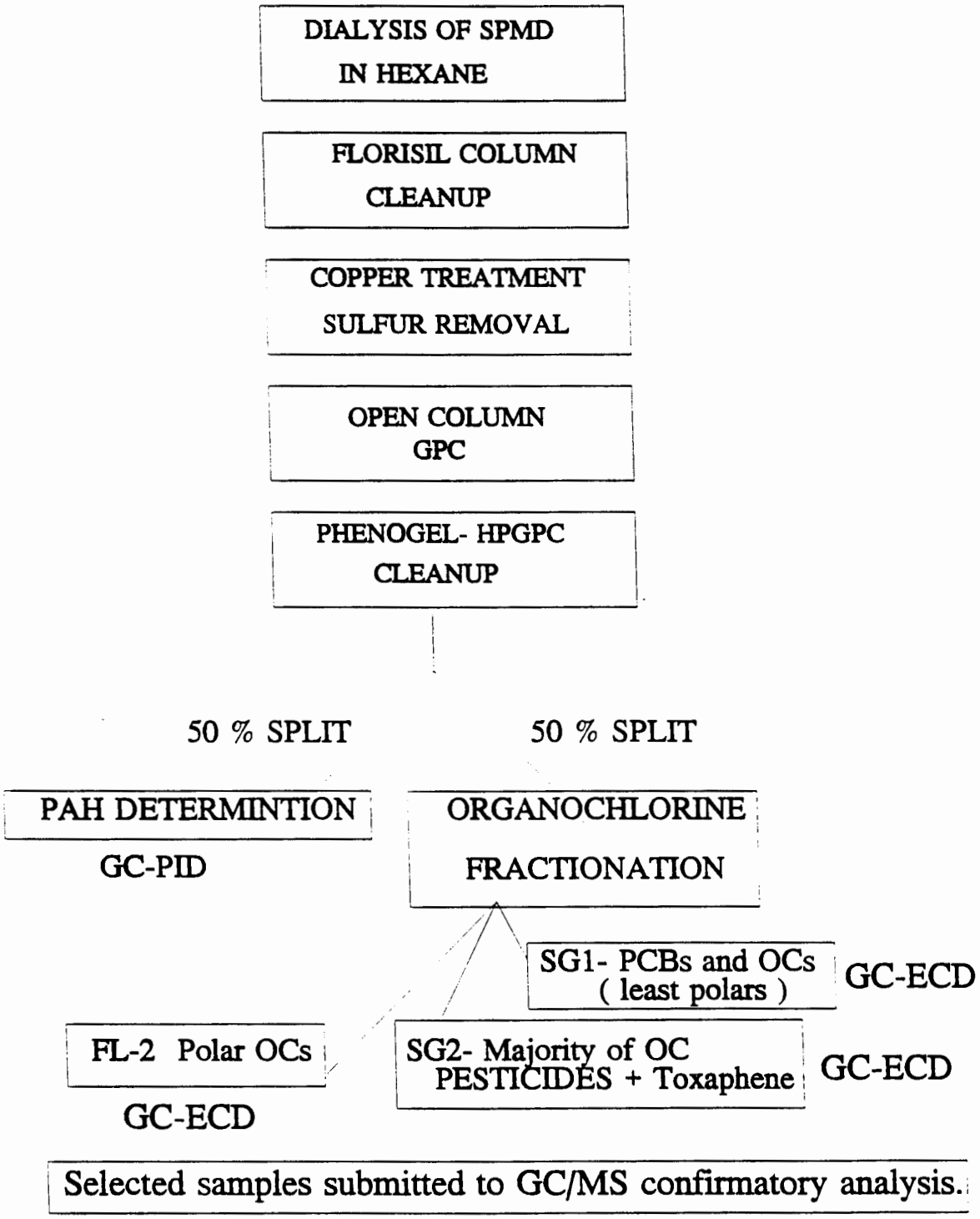
SAMPLE DESCRIPTION	Sample #	Comments
SPMD SITE SAMPLES		
Sioux City		
w/o arsenical #a	MR#5	
w/o arsenical #b	lost in field.	
Sioux #1	MR#6	
Sioux #2	MR#7	
Sioux #3	MR#8	
Sioux #4	lost in field.	
Sioux #5	lost in field.	
Sioux #6	lost in field.	
Nebraska City		
w/o arsenical #a	MR#11	
w/o arsenical #b	MR#21	
Nebraska #1	MR#12	
Nebraska #2	MR#13	
Nebraska #3	MR#14	
Nebraska #4	MR#15	
Nebraska #5	MR#16	archived
Nebraska #6	MR#22	archived
SPMD SITE SAMPLES		
Kansas City		
w/o arsenical #a	MR#30	
w/o arsenical #b	MR#31	
Kansas #1	MR#23	
Kansas #2	MR#24	
Kansas #3	MR#25	
Kansas #4	MR#32	
Kansas #5	MR#33	archived
Kansas #6	MR#34	archived
Glasgow		
w/o arsenical #a	MR#37	
w/o arsenical #b	MR#46	
Glasgow #1	MR#38	
Glasgow #2	MR#39	
Glasgow #3	MR#40	
Glasgow #4	MR#41	
Glasgow #5	MR#42	archived
Glasgow #6	MR#47	archived
Hermann		
w/o arsenical #a	MR#57	
w/o arsenical #b	MR#58	
Hermann #1	MR#48	
Hermann #2	MR#49	
Hermann #3	MR#50	
Hermann #4	MR#51	
Hermann #5	MR#59	archived
Hermann #6	MR#60	archived

MISSOURI RIVER SPMDs- SAMPLE DESCRIPTION AND NAMES

Environmental Chemistry Group- USDI NFCRC

SAMPLE DESCRIPTION	Sample #	Comments
LABORATORY CONTROLS-		
Process Blank for Set #1	MR#1	
SPMD Lab Blank Control #1	MR#2	
Process Blank for Set #2	MR#9	
SPMD Lab Blank Control #2	MR#10	
Process Blank for Set #3	MR#17	
SPMD Lab Blank Control #3	MR#18	
Process Blank for Set #4	MR#26	
SPMD Lab Blank Control #4	MR#27	
Process Blank for Set #5	MR#35	
SPMD Lab Blank Control #5	MR#36	
Process Blank for Set #6	MR#43	
SPMD Lab Blank Control #6	MR#44	
Process Blank for Set #7	MR#52	
SPMD Lab Blank Control #7	MR#53	
FIELD BLANKS-		
Sioux City Day 0 -	MR#3	
Sioux City Day 28-	MR#4	
Nebraska City Day 0 -	MR#19	
Nebraska City Day 28-	MR#20	
Kansas City Day 0 -	MR#28	
Kansas City Day 28-	MR#29	
Glasgow Day 0 -	MR#54	
Glasgow Day 28-	MR#45	
Hermann Day 0 -	MR#55	
Hermann Day 28-	MR#56	

ANALYICAL SCHEME FOR MISSOURI RIVER SPMDs



National Fisheries Contaminant Research Center
U.S. Fish and Wildlife Service
4200 New Haven Rd, Columbia, Missouri 65201

Final Laboratory Report FY-93-30-37

GC/MS ANALYSES OF DIALYSATES FROM SPMD SAMPLING DEVICES DEPLOYED IN THE MISSOURI RIVER

NFCRC Work Unit #30063

September 8, 1993

Submitted by:	Approved By:	Approved By:
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To: Dr. J. Petty

Subject: Results of full-scan GC/MS analyses of dialysates from SPMD sampling device sets deployed in the Missouri River.

Sample History: On August 15th, 1993, five samples were received from Dr. C. Orazio:

Sample	Fraction
MR-29 Kansas City Field Blank	HP-GPC only*
MR-32 Kansas City	SG2
MR-32 Kansas City	Ag-Column
MR-32 Kansas City	HP-GPC only*
MR-39 Glasgow	HP-GPC only*

*Note: HP-GPC only actually refers to dialysis/florisil/open column GPC/HP-GPC.

The sample extracts were received at a volume of about 100 μL in Chromacol semi-conical vials and were previously screened using GC/PID/FID/ECD by the Environmental Chemistry Branch.

The descriptions were entered into a sample log.

The following information was requested of the MS section:

HP-GPC only extracts-

fluorene, phenanthrene, fluoranthene, pyrene, chrysene, dieldrin, heptachlor epoxide, hydroxychlordane, chlordanes, chlordene, and 7 to 10 of the most prominent peaks.

Ag-Column-

fluorene, phenanthrene, fluoranthene, pyrene, chrysene, and characterization of pattern of peak clusters eluting throughout the chromatogram.

SG2-

heptachlor epoxide, technical chlordane components, dieldrin, chlordene, and the most prominent peaks.

Quantitative data was specifically not requested at this time.

Analytical Preparation Methods Summary:

A total of 5000 ng of the instrumental internal standard, S101R-1, was added to each vial by using 10 μL of D_{14}-labeled p-terphenyl at 500 pg/μL nonane. The final volume of all of the sample extracts was ~100-150 μL isooctane.

Samples extracts were analyzed by full-scan gas chromatography-quadrupole mass spectrometry, monitoring a mass window from m/z 35 to 700 during the chromatographic separation.

This sample set was analyzed immediately after a set of priority pollutant polycyclic aromatic compound standards was analyzed (standards S152W-1 through S156W-1). One additional standard S21W-1, NCBP-88 organochlorine pesticides at 4ng/ul, was also prepared and spiked with instrumental internal standard.

Gas Chromatography and Mass Spectrometry

Instrumentation GC/MS analysis was performed using a HP 5890 Series II gas chromatograph interfaced to a Finnigan-4023 quadrupole mass spectrometer. An HP 7673 autosampler was used to introduce 2 of ~100μL of the enriched extract onto a 5 m x 530 μm deactivated fused silica retention gap via a cool on-column injection technique. The analytes of interest were separated on a 60 m x 250 μm DB-5 capillary column with an initial hold of 1 min at 60°C followed by a single linear ramp to 300°C at 5°C/min, and held for 15 min. The carrier gas was He maintained at 40.0 psig with an initial linear velocity 35cm/sec. The analytical column was connected to the MS by a 1 m x 250 μm deactivated fused silica transferline capillary maintained at 300°C. All column-to-column connections were made using fused silica press-tight connectors.

General Detection Procedure Full-scan range from m/z 35 to 700 was scanned 0.95 sec with a reset time of 0.05 sec. Acquisition began just after the elution of the majority of the solvent, and continued until the completion of the GC temperature program. Compounds were detected either as peaks in the reconstructed-ion chromatogram (RIC), as peaks in narrower mass ranges (35-100, 100-200, 200-300, 300-400, 400-500, 500-600, 600-700) or as mass chromatograms.

Resolution Column performance was verified by analyzing quantitative standards. Similarly, the Relative Retention Times (RRTs) for all standard compounds were evaluated with respect to labeled internal standards.

The quadrupole mass spectrometer was tuned daily to give unit mass resolution.

Criteria for Confirmation: For the positive identification of a particular compound, or group of co-eluting isomers, the following criteria must be met: The peak areas of the principal ion responses must be greater than thrice the background noise and must occur at relative RRTs (corresponding to a qualitative standard analysis) within 0.5%. The background-subtracted spectrum of a peak must indicate a distinctive mass fragmentation pattern (as determined by the experience of the analyst) whose ion responses must be chromatographically correlated and are in the appropriate relative abundances. Whenever interfering compounds are detected mass spectra of co-eluting compounds are subtracted to enable interpretation as necessary.

Quantitation of Analytes: Quantitation was specifically not requested at this time. If requested, a calibration curve describing the response of each polycyclic aromatic compound or organochlorine pesticide standard to that of a labeled procedural or instrumental internal standard may be used.

Calculation of method efficiency (recovery): To account for variations in GC/MS analysis, a known amount of instrumental internal standard was spiked into the final extract and used to compare the amounts of compounds recovered in the final extract. In instances where procedural internal standards were used, and if so requested, the efficiency of the extraction and cleanup procedures may be measured by comparing the quantity of the procedural internal standards detected in the final isolated extract (awaiting instrumental analysis) with the quantity spiked into the sample at the beginning of the dialysis or extraction step.

Results and Discussion:

General Considerations for GC/MS Analysis

Samples were analyzed in one set of 5 samples, following the injection sequence of the priority pollutant PAH standards, and included S21W-1 and organochlorine pesticide standard to assist in determining the relative retention times of potentially occurring compounds.

Summary of Analytical Results:

MR-29 Kansas City Field Blank (HP-GPC only*)

The early portion of the chromatogram, from twelve to thirty minutes, contains predominately C_6 to C_{12} aldehydes and ketones. Of interest is the tentative identification of bromoheptanol, which was not found in any other sample. After thirty minutes the RIC of the field blank was dominated by elution of from C_{20} to C_{35} alkanes and C_{18} esters. Traces (< 1 ng) of phenanthrene, anthracene, and alkyl phenanthrenes were also detected.

MR-32 Kansas City (SG2)

The following compounds detected by GC/ECD were confirmed by GC/MS: heptachlor epoxide, chlordanes, trans- and cis-nonachlor, p,p'-DDE, dieldrin, alpha-chlordene.

MR-32 Kansas City (Ag-Column)

The following compounds detected by GC/PID and GC/FID were confirmed by GC/MS: fluorene, phenanthrene, fluoranthene, pyrene, chrysene.

Characterization of the pattern of very large peak clusters eluting throughout the chromatogram: the pattern consists of alkane/alkenes and have been previously observed in blanks from the silver-column.

MR-32 Kansas City and MR-39 Glasgow (HP-GPC only*)

The following compounds detected by GC/PID, GC/FID and GC/ECD were confirmed by GC/MS: fluorene, phenanthrene, fluoranthene, pyrene, chrysene, dieldrin, heptachlor epoxide, hydroxychlordane, chlordanes, trans- and cis-nonachlors, and alpha-chlordene. Once again, the most prominent peaks consisted of from C_{20} to C_{35} alkanes and C_{18} esters.

Investigation of much less prominent peaks led to the tentative identification of: trifluralin, pentachloroanisole, chlorpyrifos, penoxaline (Prowl), and tetrabromo- and pentabromodiphenylethers.

Date Prepared: 10/19/87

Date Revised: 08/18/88

PROCEDURE FOR ANALYSIS OF ORGANOCHLORINE CHEMICAL RESIDUES IN FISH TISSUES

A. Composition of a Sample Set:

Because gel permeation chromatography (GPC) is an important step in the overall enrichment scheme, and because the GPC instrument has only 23 sample loops, sample sets are limited to 23 samples. This number includes the accompanying quality control (QC) samples. Each sample set is comprised of the following.

1. A reagent blank consisting of 40.0 g anhydrous Na_2SO_4 (prepared as per SOP C5.8). This reagent blank is extracted and enriched by procedures identical to those used for all other samples, i.e. rotary evaporation, GPC, Florisil and silica gel.

2. One 10.0 g sample of positive control fish with environmentally incorporated organochlorine residues (Chemistry # 203C). Acceptable recoveries are ± 2SD of the previously established mean residue concentrations.

3. One recovery efficiency and elution behavior ^{14}C spike sample. This sample consists of a 10.0 g aliquot of negative control grass carp (Chemistry # 152C) spiked with 1.00 mL of three radiolabeled organochlorine compounds. The spikes are administered to the fish sample at the top of the extraction column. The spikes consist of 130,000 dpm of ^{14}C-Dieldrin, 125,000 dpm of ^{14}C-2,4,5,2',4',5'-hexachlorobiphenyl and 110,000 dpm of ^{14}C-p,p'-DDT (use 1.0 mL of each solution). Similar 1.00 mL aliquots of each spiking solution are put into individual scintillation vials and counted (see SOP C4.74). The radiometric recoveries are checked after some of the individual enrichment steps; if the cumulative losses are greater than 20%, and the losses cannot be satisfactorily explained, the sample set is reextracted. Read further for details.

4. One recovery efficiency spike using representative "cold" pesticides and PCBs is run. This 10.0 g sample is composed of negative control grass carp (Chemistry # 152C). The sample is spiked with 1.00 mL each of Pest QC Mix and Aroclor 1254 (see Table 1 for spike concentrations). Acceptable recoveries are ± 25% of added levels.

5. Every fifth sample set, a separate negative control grass carp (Chemistry # 152 C) 10.0 g sample will be spiked with 1.00 mL of a 5.00 µg/mL toxaphene solution and will be analyzed for toxaphene by GC/ECD. Acceptable toxaphene recoveries are ± 2SD of previously established mean recovery.

6. One unspiked 10.0 g aliquot of negative control grass carp (152C) is analyzed in each sample set for background levels.

7. One of the "unknown" environmental 10.0 g samples is extracted, enriched and analyzed in duplicate.

8. The remainder of the 23-sample set is comprised of "unknown" environmental samples. Seventeen "unknown" samples are run in each sample set. (Not including the duplicate sample)

B. Extraction

1. Use Sample Extraction Data Sheet (OC1) to list samples and other pertinent information.

2. Mix 10.0 g ground fish tissue with 40.0 g anhydrous Na_2SO_4 (SOP C5.8). Calibrate balance (Mettler PL 1200) according to SOP C4.8 and record information in NFCRC #29 Instrument Logbook. Let sample air dry, then mix it to a powder using stainless steel rods rinsed with acetone and petroleum ether (p.e.).

3. Set up a cleaned (SOP C5.7) glass extraction column (30 cm x 2 cm id, with a 200-mL reservoir) fitted with a removable Teflon stopcock (SOP C5.72). Place a pledget of glass wool and anhydrous Na_2SO_4 (1-2 cm) over stopcock. Rinse column and stopcock with acetone then p.e.

4. When each sample is dry, pour it into the column. Spike QC samples at this point. Rinse sample mixing container with CH_2Cl_2 (2X 5 mL) and pour rinsings on column allowing each rinse to drain into sample before adding the next rinse. Cover sample with 1-2 cm of anhydrous Na_2SO_4. Rinse column walls with 1-2 mL of CH_2Cl_2 and allow the rinse to drain into the sample. Extract sample with 200 mL CH_2Cl_2 adjusting flow rate to 3-5 mL/minute, collecting the eluate in a cleaned (SOP C5.7) 250-mL double reservoir flask.

5. After extraction, rinse Teflon stopcock tip with 1-2 mL of 1:1; v/v; Cyclohexane/CH_2Cl_2 (GPC Solvent) as a keeper.

6. Strip CH_2Cl_2 from the lipid by rotoevaporation (SOP C4.9) in ambient temperature water bath. Reduce extract volume to about 2-4 mL.

7. After CH_2Cl_2 removal, the upper flask chamber walls are rinsed with GPC solvent. Allow rinse to descend to lower chamber, then dilute lipid concentrate to 10.0-mL mark on flask. Place rinsed (acetone and p.e.) Teflon stoppers in flask openings. Use Teflon stoppers between all steps to preserve samples.

8. Measured portions of the lipid extract are used for GPC fractionation and % lipid determination.

C. Percent Lipid Analysis

1. Use Percent Lipid Content Data Sheet (OC3) to list samples and other pertinent information.

2. Calibrate balance (Mettler HL32 SOP C4.67) and record information in NFCRC #28 Instrument Logbook. Accurately (to the nearest 0.001 g) weigh the empty lipid vials and record weights on data sheet.

3. Using volumetric pipette, transfer measured aliquot (typically 2.00 mL) of the lipid extract to weighed lipid vial. Reinsert Teflon stopper into flask immediately after withdrawing aliquot.

4. Slowly evaporate solvent overnight at 70-80°C using heating block inside exhaust hood.

5. Calibrate balance (Mettler HL32 SOP C4.67) and record information in NFCRC #28 Instrument Logbook. Reweigh lipid vials and use the following equation to determine % lipid for each sample.
% lipid= lipid wt/sample wt x sample extract vol/lipid vol used x 100

D. Preparation for GPC enrichment.

1. Mix sufficient GPC solvent to fill reservoir.

2. Make sure battery pack is turned on and that the GPC controller is plugged into the pack. Turn "Power" on, turn "Pump" on, turn RUN/LOAD switch to RUN.

3. Press "Pump enable" to start pumping solvent through system. (If GPC has not been used for over one week, lift solvent reservoir to top of GPC to prime the lines. Watch for air bubbles to travel through solvent line into first 4-way valve, then set solvent reservoir back on shelf by GPC.)

4. Switch column on-line by pushing column in/out switch to out position to rewet column.

5. Turn on the U.V. Absorbance Detector to warm up before using.

6. If cleaning GPC column, follow instructions in SOP C4.7 Section K.

7. To wash sample loops and collect lines, set dump to 3 minutes, collect to 3 minutes, and wash to 0 minutes, set RUN/LOAD switch to run, set column in/out switch to in (takes column off line), set terminal to #23, set index to loop #0 and push autostart. This will automatically wash all the loops and collect lines.

8. Calibrate GPC as per SOP C4.7.

E. Gel Permeation Chromatography (GPC).

1. Use GPC Data Sheet (OC4) to list samples and other pertinent information.

2. Use 8.0 mL of lipid extract to fill GPC's 5.0-mL loops. Rinse load lines with GPC solvent between each sample. Sequentially load samples as listed on GPC Data Sheet. Note: Filter lipid concentrate through stainless steel filter that is attached to the loading syringe.

3. Note: It is critical to dilute all samples with % lipid greater than 10% (rounded to nearest %) so as to put a maximum of only 500 mg lipid on each GPC loop. For example: sample has 17.9% lipid, use 5.0 mL of the original 10.0 mL and dilute to 9.0 mL; 5.0 mL of extract has 0.9 g of lipid. When diluted to 9.0 mL, the dilution has 0.5 g of lipid in the 5.0 mL GPC sample.

4. Set dump and collect times according to the results of the calibration (determined in step D8). Index to loop 0, set terminal to the appropriate number of samples, put column on line, turn RUN/LOAD switch to RUN and press autostart.

5. Collect desired pesticides and chlorinated hydrocarbon residues in cleaned (SOP C5.7) and labeled 250-mL double reservoir flasks.

6. Strip extra solvent from samples by rotoevaporating (SOP C4.9) in a ambient temperature water bath. Reduce extract volume to 1-2 mL.

7. Bring ^{14}C spike sample to 10.0 mL volume in flask using p.e. Use a 1.00 mL volumetric pipette for transfer to scintillation vials for ^{14}C counting (SOP C4.74). Record dpm's, calculations and % recoveries on ^{14}C Quality Control Data Sheet (QC2). Recoveries obtained at this step will be composite of all three radiolabeled compounds.

F. Florisil Enrichment and Fractionation.

1. Use Florisil Data Sheet (QC5) to list samples and other pertinent information.

2. Fisher Florisil (60-100 Mesh) is cleaned by annealing at 450°C for 10 hours to remove trace organic contaminants. Then activate at 130°C for at least 24 hours before using.

3. Cleaned (SOP C5.7) Florisil columns (30 cm x 1 cm id, with a 75-mL reservoir) are fitted with a Teflon stopcock (SOP C5.72). Place a pledget of glass wool and anhydrous Na_2SO_4 (1-2 cm) over stopcock then rinse with acetone then p.e. Calibrate balance (Mettler PL 1200) according to SOP C4.8 and record information in NFCRC #29 Instrument Logbook. Activated Florisil (5.0 g) is dry-packed, covered with anhydrous Na_2SO_4 then immediately rinsed with 20 mL p.e. and the p.e. rinse effluent is discarded. The p.e. is stopped 1-2 cm above Na_2SO_4. Rinse stopcock tip with p.e. and discard.

4. Transfer all the concentrated GPC eluates (except ^{14}C spike sample) to the column using a baked transfer pipette, allowing extract to just drain into the Na_2SO_4. Rinse flask twice with 1-2 mL of p.e.

and transfer rinses to column, each time allowing liquid level to descend just to Na_2SO_4 level.

5. For the radiolabeled spike, use a volumetric pipette to transfer 5.00 mL of the 10.0 mL volume to top of the Florisil column.

6. Florisil parameters (appropriate elution volume) were previously determined for the 5% fraction by following step F.3 then spiking the column with 1.00 mL each of Pest 1 x 1/20 and PCB 1 x 1/20 (see Table 2). Another column was spiked with 1.00 mL of PCB 1254 (5.00 µg/mL). The 5% diethyl ether/ p.e. fraction volume was determined by eluting with 60 mL and collecting the 40 to 60 mL portion in 5-mL fractions. The solvent volume needed was determined by G.C. analysis.

7. Florisil parameters (appropriate elution volume) were previously determined for the 40% fraction by following steps F.3, then spiking the column with 1.00 mL of Pest 2 x 1/20 (see Table 2). Use the predetermined volume of 5% diethyl ether/ p.e. (determined in step F6) and then elute with 80 mL of 40% diethyl ether/p.e. collecting the 50 to 80 mL portion in 5-mL fractions. Determine 40% fraction solvent volume by G.C. analysis.

8. Non-polar and moderately polar pesticides and chlorinated hydrocarbon residues are eluted with predetermined volume of 5% diethyl ether/p.e. (from step F6) solution.

9. Very polar pesticides and chlorinated hydrocarbon residues are eluted with predetermined volume of 40% diethyl ether/p.e. (from step F7) solution.

10. The fractions are collected separately in cleaned (SOP C 5.7) 125-mL double reservoir flasks. 1-2 mL of hexane is added to the 5% fraction and 1-2 mL isooctane is added to the 40% fraction to minimize loss of volatile pesticides during rotoevaporation.

11. Ethers are removed by rotoevaporation (SOP C4.9) in a ambient temperature water bath. Reduce extract to a volume of 1-2 mL.

12. Aldrin (for use as a reference peak) is added to the 40% fraction following solvent reduction. Use 100 µL of 1.00 µg/mL Aldrin for a final concentration of 0.02 µg/mL. Then bring samples (40% fx) to 5.0 mL volume in the flask with isooctane. Use baked transfer pipette to load 1 mL of extract into baked autosample vials for GC analysis. Transfer remainder of sample to baked test tube and mark sample level with felt tipped pen, cover mark with Scotch Tape and store in refrigerator in Room 25. The top of the mark should identify the bottom of the solvent meniscus.

13. The 5% Florisil fraction is left in Teflon stoppered flasks for silica gel fractionation.

14. Bring ^{14}C spike samples (both 5% and 40% fraction) to 5.0 mL volume. Use hexane for 5% and isooctane for 40%. Use a 1.00 mL volumetric pipette for transfer to scintillation vials for ^{14}C counting (SOP C4.74). Record the dpm's, calculations and % recoveries on ^{14}C Quality Control Data Sheet (OC2). The 5% fraction should have hexachlorobiphenyl and the p,p'-DDT in it and the % recoveries determined for it will be a composite of the two. The 40% fraction should only have the Dieldrin.

G. Silica Gel Enrichment and Fractionation

1. Use Silica Gel Data Sheet (OC6) to list samples and other pertinent information.

2. Silica gel (Silica gel 60, 70-230 mesh ASTM, E Merck) has been previously prepared as prescribed in SOP C5.67 Section 4. Then activate at 130°C for at least 24 hours before column preparation.

3. Cleaned (SOP C5.7) Florisil columns (30 cm x 1 cm id, with a 75-mL reservoirs) are fitted with removable Teflon stopcocks (SOP C5.72). Place pledgets of glass wool and anhydrous Na_2SO_4 (1-2 cm) over the stopcocks then rinse with acetone then p.e. Calibrate balance (Mettler PL 1200) according to SOP C4.8 and record information in NFCRC #29 Instrument Logbook. Activated silica gel (5.0 g) is dry packed, covered with 1-2 cm of anhydrous Na_2SO_4 then is immediately rinsed with 20 mL hexane and the hexane rinse effluent is discarded. The hexane is stopped 1-2 cm above Na_2SO_4. Rinse stopcock tip with hexane and discard.

4. Silica gel parameters (appropriate elution volume) were previously determined for the PCB fraction by following step G3 then spiking the column with 1.00 mL of PCB 1 x 1/20 and PCB 1254 (5.00 µg/mL). Column is eluted with 50 mL of 0.5% benzene/hexane collecting the 30 to 50 mL portion in 5 mL fractions. The solvent volume required is then determined by G.C. analysis.

5. Silica gel parameters (appropriate elution volume) were previously determined for the Pesticide fraction by following step G3 then spiking the column with 1.00 mL of Pest 1 x 1/20 and Toxaphene (5.00 µg/mL). Column is then eluted with the predetermined volume of 0.5% benzene/hexane (determined in step G4) and then elute with 70 mL 25% diethyl ether/hexane collecting the 50 to 70 mL portion in 5 mL fractions. Determine the Pesticide fraction solvent volume by G.C. analysis.

6. For all except the ^{14}C spike sample, transfer the concentrated 5% Florisil fraction eluant (using baked transfer pipettes) to the columns for fractionation. Allow eluant to just drain into the Na_2SO_4. Rinse flask twice with 1-2 mL of hexane and transfer each rinse to column, allowing the liquid level to descend just to Na_2SO_4 level.

7. For the radiolabeled spike, use a volumetric pipette to transfer 3.00 mL of the 5.0 mL volume to the top of the silica gel column.

8. The PCB fraction is eluted with the predetermined volume of 0.5% benzene/hexane (from step G4) solution.

9. The Pest fraction is eluted with the predetermined volume of 25% diethyl ether/hexane (from step G5) solution.

10. Both fractions are collected in cleaned (SOP C 5.7) 125-mL double reservoir flask. 1-2 mL isooctane is added to each fraction and rotoevaporated in a ambient temperature water bath to 1-2 mL.

11. Bring ^{14}C spike samples to 5.0 mL volume using isooctane. Use a 1.00 mL volumetric pipette for transfer to scintillation vials for ^{14}C counting (SOP C4.74). Record dpm's, calculations and % recoveries on ^{14}C Quality Control Data Sheet (QC2). The PCB fraction should have hexachlorobiphenyl and the Pest fraction should have p,p' DDT in them.

12. Aldrin (for use as a reference peak) is added to both PCB and Pest fraction samples following solvent reduction. Use 100 µL of 1.00 µg/mL Aldrin for a final concentration of 0.02 µg/mL. Then bring samples to 5.0 mL volume and transfer with baked transfer pipettes to baked autosampler vials for GC analysis. Transfer remainder of the samples to baked test tube and mark sample level with felt tipped pen, cover mark with Scotch Tape and store in refrigerator in Room 25. The top of the mark should identify the bottom of the solvent meniscus.

H. High Resolution Capillary Gas Chromatographic Analysis by Electron Capture Detection (GC/ECD) (see SOP C4.21).

1. Capillary columns are optimized using linear velocity ($\bar{\mu}$), theoretical plates ($n_{1/2}$ & $n_{5\sigma}$), Liberti's Asymmetry factor (A_s) and NFCRC's Asymmetry factor ($n_{5\sigma}/n_{1/2}$). This data is recorded in the calibration section of the NFCRC Instrument Logbook.

The following pieces of data must be determined and recorded in the appropriate instrument log: column pressure, dead vol time (t_o), $t_{lindane}$, t_{aldrin}, avg linear velocity ($\bar{\mu}$), Aldrin ($N_{5\sigma}$). All other data is optional for trouble shooting only.

$\bar{\mu}$ = L(column length in cm)/t_o (retention time of air peak in sec)

Theoretical plates:

($n_{1/2}$) denotes average number of theoretical plates/ column

$$n_{1/2} = 5.54\ (t_{aldrin}/w_{1/2})^2$$

where: t_{aldrin} is the retention time of the aldrin peak (min.)
$w_{1/2}$ is the peak width (min.) at half height

($n_{5\sigma}$) denotes the average number of theoretical plates/column

$$n_{5\sigma} = 25(t_{aldrin}/w_{4.4\%})^2$$

where: $w_{4.4\%}$ is the peak width (min) at 4.4% of the peak height

Liberti's Asymmetry Factor:

$$A_s = \frac{a+b}{(a+b)-(a-b)}$$

where a and b are the baseline half widths measured from the perpendicular drawn through the peak maximium

NFCRC Asymmetry Factor = $n_{5\sigma}/n_{1/2}$

All equations are taken or derived from those in:

M.L. Lee, F.J. Yang and K.D. Bartle. Open tubular column gas chromatography. John Wiley and Sons, Inc, New York, NY. (1984).

G. Gorettio and A. Liberti. J. Chromatogr. 161,89 (1978).

B.A. Bidiingmeyer and F. Vincent Warren Jr. "Column efficiency measurement." Anal Chem. 56, pg 1583A. (1984).

2. Before each set of samples the above parameters (that are specified as required) are determined, using Varian ECD Test Sample, to ensure column efficiency. The data is recorded in the NFCRC Instrument Logbook. In addition, record the Area Response/μl injected for the aldrin peak.

   The $n_{1/2}$ results are used to evaluate the optimum chromatographic potential of the specified chromatographic system. This parameter is least affected by overloading (due to loss of column coating during maturation) or adsorption and dead volume effects that cause peak tailing. This parameter is obtained graphically using an Alltech Peakometer, Alltech Assoc., Deerfield, Ill.

   The $n_{5\sigma}$ (number of theoretical plates at 5 sigma, 4.4% of the peak height above the baseline) results are much more indicative of peak asymmetry. It is our belief that $n_{5\sigma}/n_{1/2}$ is easily determined after graphic measurements of $n_{5\sigma}$, again using the Alltech Peakometer. To determine $n_{5\sigma}$: Measure the peak height in cm. Multiply this H(cm) by 2*(0.956) and then use the peakometer to determine the peak width at 4.4% above baseline.

3. Column types used for each organochlorine fraction:

a. Pesticide fraction from silica gel: 25m bonded OV-17 fused silica capillary, 0.25 mm ID, 0.25 μm film thickness with a 1m, 0.32 mm I.D. uncoated, deactivated (J&W Scientific) fused silica column as retention gap.

b. 40% fraction from Florisil and PCB fraction from silica gel: 30m DB-5 (bonded phenyl,methyl silicone) fused silica capillary, 0.25 mm I.D., 0.25 um film thickness with a 1 m, 0.32 mm I.D. uncoated, deactivated (J&W Scientific) fused silica column as retention gap.

4. Varian GC Conditions

a. Capillary injection systems use modified split/splitless liners in the direct injection mode with a septum purge of 4 mL/min of H_2.

b. Capillary flow rates are measured at 60°C as linear velocities.

c. The GC oven temperature is held for 2 min at 60°C then programmed at 4°/min to 240°C where it is held for 8 min.

d. The GC injection temperature is 220°C and the detector temperature is 320°C.

e. The total detector flow (H_2 carrier + N_2 make-up gas) is 30 mL/min.

f. The detector is a ^{63}Ni electron capture with linearizer.

g. A Varian Series 8000 Autosampler is used for sample injection. Standards and sample order of injection information is recorded in the NFCRC Sample Tracking Instrument Logbook. A typical autosampler run would have 65 total injections with 40 standard/QC and 25 samples. The standard and samples would be randomly intermixed throughout the run.

h. The GC is interfaced with a Nelson Analytical Chromatography System for data collection and reduction.

I. Chromatographic Data Reduction

1. Use the measured peak retention times for each representative calibration standard mixture (Pest 1; Pest 2; PCB 1; Aroclors: 1248, 1254 and 1260; and Toxaphene) to set up the Nelson Analytical Chromatography System calculation method. In the method include each component's retention time, concentration and name. Calibrate each standard using the appropriate method to determine each component's relative retention time vs Aldrin for peak identification. Set Aldrin relative retention time to equal 10.0.

2. Test all calculation method files for peak detection accuracy and interference from other calibrated components within a given enrichment fraction.

3. Use calibrated methods to identify target component peaks in all the samples and spikes.

4. Use the regression program to calculate target component concentrations in the samples and spikes. Then determine the spike sample(s) per cent recoveries as follows:

$$\% \text{ Recovery} = \frac{\text{measured background corrected spike conc.}}{\text{concentration of spike solution}} \times 100\%$$

J. Standards

1. Use SOP # C5.4 for logging in of Analytical Standard Materials. Enter information in the Chemical Standard (Neat and High Stock Solutions) Record Book kept in Room 14.

2. Use EPA "Preparation of Concentrated Stock Standards" (OCSTD1) form from the EPA "Manual for Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples" for weighing and diluting "neat" compounds.

3. Calibrate balance (Mettler HL32 SOP C4.67) and record information in NFCRC #28 Instrument Logbook.

4. Weigh out 10 mg of the compound into a cleaned (SOP C5.7), solvent rinsed (acetone and p.e.) test tube and diluted to 10.00 mL volume (1.0 mg/mL). Record information on OCSTD1 data sheet, in the Organic Chemical Standards Record Book and in NFCRC #28 Instrument Logbook.

5. Use OCSTD2 data sheet (EPA form "Preparation of Standards of Intermediary Concentration") for making dilutions of Concentrated Stock Standards. Also use SOP C5.4 for logging in working standard solutions. Use solvent rinsed (acetone and p.e.) volumetric pipettes and flasks for making these dilutions.

6. Use these Intermediate Standards for making "Working Stock Solutions" (Table 1). Then use "Working Stock Solutions" to make QC Spiking Mixtures (Table 2) and Analytical GC Standards.

Prepared by:

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Approved by:

Ted R. Schwartz
Chief Chemist

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Table 1. Pesticide QC Mix (for spiking, use 1.00 mL per 10.0 g.)

Compound	Conc in µg/mL
Dacthal	0.40
Dieldrin	0.40
Endrin	0.40
Hexachlorobenzene	0.40
Heptachlor	0.40
Mirex	0.40
Pentachloroanisole	0.40
Alpha BHC	0.40
Gamma BHC (Lindane)	0.40
Beta BHC	0.40
Delta BHC	0.40
Oxychlordane	0.40
Heptachlor Epoxide	0.40
trans-Chlordane	0.40
trans-Nonachlor	0.40
cis-Chlordane	0.40
o,p'-DDE	0.40
p,p'-DDE	1.00
o,p'-DDD	0.40
cis-Nonachlor	0.40
p,p'-DDD	0.40
p,p'-DDT	0.40
Methoxychlor	0.40
Toxaphene	5.00
Aroclor 1254	5.00

When GC standards are made from stock solutions, Aldrin is added at a concentration of 0.02 µg/mL as internal standard and reference peak. The reference peak is used in peak identification and to verify chromatographic response within each GC chromatogram.

All stock solutions and dilutions are made up in isooctane and stored in brown bottles.

Table 2. Stock Solutions for Gas Chromatography (used to make diluted GC Standards)

Compound	Conc in µg/mL
Pest 1	
Pentachloroanisole	1.00
Alpha BHC	1.00
Gamma BHC (Lindane)	1.00
Beta BHC	2.00
Delta BHC	2.00
Oxychlordane	1.00
Heptachlor Epoxide	1.00
trans-Chlordane	1.00
trans-Nonachlor	1.00
cis-Chlordane	1.00
o,p'-DDE	2.00
p,p'-DDE	2.00
o,p'-DDD	2.00
cis-Nonachlor	2.00
o,p'-DDT	2.00
p,p'-DDD	4.00
p,p'-DDT	4.00
Methoxychlor	5.00
PCB 1	
Hexachlorobenzene	1.00
Heptachlor	1.00
p,p'-DDE	2.00
Mirex	4.00
Pest 2	
Delta BHC	2.00
Dacthal	2.00
Dieldrin	2.00
Endrin	4.00
PCBs	
Aroclor 1242	10.00
Aroclor 1248	10.00
Aroclor 1254	10.00
Aroclor 1260	10.00
Toxaphene	
Toxaphene	10.00

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THE TREATMENT OF EXTRACTS OF ENVIRONMENTAL SAMPLES FOR REMOVAL OF ELEMENTAL SULFUR

I. General

Environmental samples often contain elemental sulfur which, when the samples are extracted, is co-extracted with the analytes. The elemental sulfur then presents analytical problems when the extracts are analyzed by gas or liquid chromatography or gas chromatography/mass spectrometry. Sediment is the sample matrix that most commonly contains elemental sulfur, but sulfur has also been found in certain benthos samples and might conceivably be present in samples of soil and aquatic plants. The Organic Chemistry Section's analytical projects proceed more smoothly when the elemental sulfur removal is preemptively accomplished rather than after its presence has been confirmed by thwarted analyses. The sulfur removal procedure described by this SOP should be a mandatory component of the enrichment schemes for all sediment samples. This procedure should also be an integral part of enrichment schemes for samples of benthos, aquatic plants, and soil unless the absence of sulfur has been documented.

II. General Procedure for Removal of Elemental Sulfur

The general procedure for the removal of elemental sulfur from sample extracts involves treatment of the extracts with balls of copper wool or of copper turnings. The copper is submerged in the organic solvent of the extracts, and the dissolved elemental sulfur reacts with the copper to form copper sulfide which appears as a dull, black plating on the copper. The copper sulfide is then removed from the extract when the balls of copper to which it adheres are removed.

III. Preparation of the Copper

The best copper for this application is copper turnings, light (MC/B Manufacturing Chemists). Fine copper wool is also usable. The copper strands must be rolled into balls of the appropriate size. The size of copper ball that is appropriate for a sample is governed primarily by the size of the opening in the sample container through which the copper ball must be inserted and withdrawn. Extracts containing a lot of elemental sulfur are often treated with more than one copper ball. It is best, for this reason, to treat extracts with copper when the sample container is a flat bottom flask with a 24/40 ground-glass joint. Copper balls of a diameter greater than 1 cm can be used, thereby reducing the number of copper balls needed per sample.

Use scissors to cut the quantity of copper strands needed for each ball. Copper balls made from fewer long strands are preferable to those made from more short strands. Roll the strands into balls on the benchtop.

Submerge the copper balls for 20 seconds in a beaker containing 0.75 Molar nitric acid. (The actual concentration of the acid need only be approximate; 50 mL of concentrated nitric acid diluted to 1 L with deionized water is an adequate approximation.) While the copper balls are submerged, use forceps to compress them and force out any air bubbles trapped in the center of the balls. After the 20 seconds have elapsed, quickly dump the acid from the beaker while holding the copper in place with the forceps. Run tap water at a high flow rate into the beaker containing the copper balls. This procedure rinses the nitric acid out of the interior of the copper balls. After the tap water has run into the beaker for 5 min, hold the copper balls in the beaker with forceps and rinse the beaker and copper balls three times with deionized water.

After the above steps have been taken, the copper balls are individually prepared and inserted into the samples. The following steps must be taken quickly to avoid getting condensation on the copper. Subsequent enrichment steps might be compromised for samples containing water introduced during sulfur removal. Pick up each copper ball with the forceps and rinse the ball and the lower part of the forceps thoroughly with acetone, then with dichloromethane. Squirt bottles should be used for these steps. After having rinsed a ball with dichloromethane, quickly insert it in the sample container.

IV. Treatment of the Extracts with Copper

Samples containing a lot of elemental sulfur will require more than one copper ball. In extreme cases, the copper will turn black almost instantly. The need for further copper treatment will be signified by copper balls that have turned entirely black, especially if the color change was instantaneous. In general, if after having been submerged in a sample extract for several hours, the copper balls are still bright and shiny, no further treatment with copper is needed. (Read this SOP further for exceptions to this general statement.)

V. Removal of the Copper from the Extract

Either forceps or hook-shaped wires can be used to remove copper balls from sample extracts. After the copper balls have been lifted clear of the liquid, the copper must be rinsed thoroughly with solvent from a squirt bottle. The copper balls will have held some of the extract inside them through capillary action, and this liquid must be rinsed back into the sample container with fresh solvent. Hexane, cyclohexane, cyclopentane, and dichloromethane are just some of the solvents that can be used for this purpose. Consult a supervisor when in doubt as to which solvent to choose. Since by rinsing the used copper balls, the volumes of the extracts are increased, it is important that the sample

containers have adequate capacity to accommodate this additional solvent. One approach to this problem is to rotary evaporate the extracts to a liquid level just sufficient to fully submerge the copper balls before initiating the sulfur removal.

VI. General Discussion

Rinsing of the copper balls with solvent during their removal from the extract sometimes dislodges copper sulfide from the surface of the strands. Visible black particulate material at the bottom of the extract signifies that this has occurred. This black particulate causes several problems during later handling of the sample. During subsequent rotary evaporation the copper sulfide material can act as boiling chips and cause bumping of the sample. Sample loss can occur. The tendency of the samples to bump during rotary evaporation can be alleviated by lowering the vacuum or the temperature at which the samples are evaporated. The copper sulfide can also cause problems by plugging up GPCs and syringes. If actually injected on a GC or HPLC, the copper sulfide can cause analytical trouble for subsequent samples. This material must be filtered out prior to GPC enrichment or instrumental analysis. If the enrichment step immediately after the sulfur removal is silica gel, Florisil, alumina, or potassium silicate chromatography, the copper sulfide is automatically filtered out by the adsorbent, and in no way interferes with the fractionation or enrichment by these methods.

Extracts that contain large amounts of biogenic material such as chlorophyll, carotene, etc., can be difficult to remove elemental sulfur from. The copper balls submerged in these samples can still be bright and shiny after 24 hours, yet the extracts often still contain a lot of elemental sulfur. It appears that the presence of the pigments somehow interferes with the copper treatment. For highly colored samples, it is usually best to wait until after preliminary enrichment steps have been taken before attempting removal of elemental sulfur or to repeat the copper treatment after the preliminary enrichment step.

Since the adoption of capillary GC and capillary GC/MS methods by this laboratory, the need for complete removal of elemental sulfur from samples has become more acute. Capillary chromatography is more sensitive to sulfur-related interferences than was packed column chromatography. For this reason, supplemental sulfur removal is often required immediately prior to instrumental analyses. Often, the copper balls are simply left in the sample container, be it an autoinjector vial or test tube, during instrumental analysis. Consult a supervisor as to whether this supplemental sulfur removal will be necessary.

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PREPARATION AND USE OF GRAVITY-FLOW GEL PERMEATION CHROMATOGRAPHY (GPC) COLUMNS

I. INTRODUCTION

An alternative to the use of automated GPC sample processing is available in the form of glass chromatography columns fitted with stopcocks and containing the GPC medium. The sample is manually applied to the column in a small amount of solvent and is washed through the chromatographic medium with measured volumes of eluant. Flow through the column is driven by the force of gravity and analytes of interest are separated from lipids and other large biogenic molecules by size exclusion into pre-established "Dump" and "Collect" fractions. Advantages of this method include simplicity of the procedure, less materials usage (solvents, GPC media, etc.), elimination of the possibility of instrument failure, and increased speed of obtaining fractionated extracts. The columns described herein can accommodate amounts of sample lipids comparable to the automated system with comparable or decreased man-hours per sample. This SOP details preparation and calibration of the column followed by sample application and fractionation.

II. REAGENTS AND APPARATUS

A. Columns: Glass, 2 cm. I.D. x 30 cm. long, with teflon stopcocks and ≥100 mL reservoirs.

B. SX-3 Biobeads: 200-400 mesh from BIO-RAD Laboratories, cat. # 152-2750.

C. Mobile Phase: 80/20 Hexane/Dichloromethane; V+V (made with UV grade or Fisher universal grade solvents)

III. COLUMN PACKING

A. Weigh 10.0 gram portions of the SX-3 biobeads into 250 mL Erlenmeyer flasks and add ~100mL of the mobile phase to each. Cover the flasks and allow the beads to soak for at least four hours to obtain maximum swelling. In the meantime, prepare a clean column for each portion. Tamp a small wad of glass wool over the stopcock in the bottom of

each column and cover it with a 1 cm. segment of 200-400 mesh glass beads.

B. After the biobeads have soaked the required period of time, transfer them to the columns. Gently pour about half the solvent off the top of the beads and into the columns. Allow this solvent to drain to within ~5 cm. of the top of the glass beads before closing the stopcocks. Slurry the beads by swirling the flasks and immediately pour the mixture into the columns. Open the stopcocks and finish quantitatively transferring the beads by rinsing the flasks with 5-10 mL portions of mobile phase and adding these to the columns. As the solvent drains and the bead beds settle, rinse adhering beads from the column sides with the 80/20 mobile phase from a pasteur pipet.

C. When the solvent has drained to within ~1 cm. of the top of the gel beds, wash the columns with an additional 100 mL fresh eluant. Close the stopcocks when the solvent drains to within a cm. or two of the top of the gel beds. Columns should be tightly covered to prevent solvent evaporation during storage and care should be taken during sample manipulations to prevent the mobile phase from draining past the top of the gel beds. Columns prepared in this way may be used indefinitely and are now ready for calibration.

IV. COLUMN CALIBRATION

A. The column described in this SOP can accommodate 0.5 mL of sample lipid. This lipid elutes in the first 27 mL of solvent and the analytes of interest elute in the 28-50 mL fraction. These fractions may be checked by diluting 0.5 mL (0.455 g.) of ACS grade triolein with the 80/20 solvent mixture to a total volume of 1.0 mL, spiking it with 50-100K counts of ^{14}C-2,2',5,5'-tetrachlorobiphenyl, and applying it to the column following the sample application procedure outlined in part V of this SOP. Both fractions are collected and a 2-mL aliquant of each is then counted by liquid scintillation to verify ≥ 95% recovery of the compound in the "collect" fraction. The lipid content of both fractions is quantified by solvent removal followed by gravimetric analysis. The "collect" fraction should contain less than 10 mg. of lipid.

B. If the above parameters are not met, a more thorough characterization must be performed. The spiked lipid is added to the column as described above. The first 25 mL may be collected in one fraction. A series of five 2-mL fractions are then collected separately, followed by two 15-mL fractions. Two mL of the 25-mL and the two 15-mL

fractions, and 0.5 mL of the five 2-mL fractions are analyzed in the scintillation counter. The remainder of each fraction undergoes solvent removal and gravimetric analysis for lipid content. Use the resultant data to establish "dump" and "collect" volumes that adhere to the parameters described above.

V. SAMPLE EXTRACT FRACTIONATION

A. Sample extracts that undergo this procedure may come from a variety of extraction methods and be composed of a variety of solvents or solvent mixtures. The objectives of the following pretreatment of the sample extract are: 1) to bring the extract volume to 1.0 mL, and 2) to approximate the solvent composition of the mobile phase as closely as possible. The following pretreatment is geared toward extracts composed of various mixtures of methylene chloride, hexane, cyclohexane, cyclopentane, isooctane, or petroleum ether. If the extract contains solvents other than these, consult the chemist in charge of the project.

The sample extract is reduced in volume by rotoevaporation to ~2 mL. The concentrated extract is transferred quantitatively with the 80/20 solvent mixture to a culture tube that is calibrated at 1 mL. Reduce the volume of the extract to approximately 0.5 mL by evaporation with dry nitrogen and *q.s.* to 1.0 mL with the 80/20 solvent.

Measure 28 mL of the 80/20 solvent in a 50-mL graduated cylinder. Transfer the sample extract to the top of the column with a pasteur pipet, taking care not to disturb the column bed. **Care should always be taken not to disturb the gel bed when applying samples or solvents.** Open the stopcock and drain the column effluent into a waste container. Rinse the sample tube with 1 mL of solvent from the graduated cylinder and add this to the column after the sample extract has drained to the top of the column bed. Repeat the rinse step twice more. After the third rinse has drained into the column bed, carefully add the remainder of the premeasured solvent. This is the "dump" fraction and is drained to waste. When this fraction has drained to the top of the column bed, shut the stopcock and replace the waste container with a clean 50-mL or 100-mL round-bottom flask. Measure and add 22 mL of the 80/20 solvent to the column and drain this fraction, the "collect" fraction, into the round-bottom flask. The cleaned sample extract may now be concentrated for further fractionation steps or procede to GC analysis.

B. Gel Permeation Chromatography separates molecules predominantly on the basis of size. The larger molecules,

such as lipids, are excluded from the pores of the resin and therefore elute first. The "collect" fraction is established such that it encompasses the elution volume of molecules of a size range corresponding to that of the analytes. After the analytes have been collected, molecules from the sample extract that are below that size range are still present on the column and must be washed off.

After the "collect"fraction has been obtained, add ~100 mL of eluant to the column and open the stopcock. Using a vacuum/pressure squeeze bulb connected to stopper that fits the top of the column reservoir, apply pressure to the column for ~ 1 minute. This compresses the gel bed and tends to remove any gas pockets or voids that may have formed in the bed. After this "wash" has drained through the column, it is ready for the next sample application.

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SEMIPERMEABLE MEMBRANE DEVICE (SPMD) CLEANUP AND PREPARATION FOR ANALYSIS

I. **Introduction** - This is a new approach to environmental contaminant monitoring and the cleanup procedure will be refined as experience is gained. The purpose of this S.O.P. is to delineate key procedural limits of the method and yet provide certain specific parameters that currently appear optimal.

II. **Preparation of glassware** - In order to reduce the possibility of the introduction of laboratory contaminants into sample extracts during sample processing or handling, the following procedure is used to clean all glassware:

1. Wash all glassware with laboratory detergent and tap (well water) water. Rinse thoroughly with tap water ($\geq$ 3 times).
2. Rinse each piece of glassware three times with 1 N HCl.
3. Rinse thoroughly with deionized water ($\geq$ 3 times).
4. Rinse three (3) times with acetone.
5. Rinse three (3) times with hexane.
6. Air dry.
7. Bake in the annealing oven at 475 ^{o}C for eight hours.
8. As soon as the glassware is removed from the oven, cover all openings of the glassware with solvent-rinsed (acetone/hexane) aluminum foil and store in drawers or other dust-free areas.

9. Immediately prior to use, rinse each piece of glassware with cyclopentane three (3) times.

Note: Glassware that cannot be annealed, should be rinsed with cyclopentane six (6) times immediately prior to use.

III. **Preparation of SPMDs for dialysis** - When the SPMD is received from field or laboratory exposures, they may have algae, sediment, inorganic salts and other material coating their exterior surface. To prevent this material from contaminating the dialysate, a removal or cleanup step is usually required before dialysis. (Note: Do not touch the SPMD membranes with your hands prior to the following hexane rinse procedure.)

1. If the SPMDs are sealed in an amber sample jar (volume = 500 mL), the jar is used in the first preparation step. (Also applies to freshly prepared SPMDs; place in a clean 500 mL amber jar). Measure 250 mL of nanograde hexane and pour into the sample jar and then tightly close with a Teflon-lined cap. Shake the jar 20 - 30 seconds and immediately discard the hexane.

2. Afterwards the SPMDs are placed in a large flat stainless steel pan and using running tap water and a brush and/or hands, remove all remaining surface debris.

Note: If the SPMDs have an additional seal above the end seals, cut it off and discard. This portion of the

SPMD is usually covered with debris that cannot be easily removed.

3. Drain the water off the SPMDs and swish them in a glass tank containing 1 N HCl for a few seconds (≤ 30 sec.).

4. Thoroughly rinse the SPMDs with tap water to remove acid.

5. Remove all surface water from the SPMDs, using rinses of isopropanol followed by acetone. Let the rinse solvent evaporate before dialyzing, by laying the SPMDs on a piece of solvent-rinsed aluminum foil for a few minutes.

6. At this time the SPMDs are counted and closely inspected for holes. A sample set may consist of a total of 7 SPMDs. When possible, six (6) SPMDs are dialyzed with hexane (nanograde) as a single batch sample. The seventh SPMD is used to generate a quality control recovery spike as described in Part VI, 3.

IV. **Dialysis** - Canning jars, 1 and 2 quart size, with solvent-rinsed aluminum foil under the screw type lids to create a tight seal are used for the dialysis step. The amount of hexane used for dialysis depends on the total mass of membrane and lipid. A 68" SPMD filled with ~ 2 mL lipid, requires 250 mL hexane, thus 1 bag (68" SPMD) requires 250 mL, 2 bags requires 500 mL, etc. Dialyze the SPMDs 48 hours. After 48 hours, the membranes are removed from the jar and usually discarded following proper disposal

procedures. The dialysate is quantitatively transferred (using three 3 to 5 mL rinses of hexane) into a round bottom flask equipped with a rotary evaporation trap and reduced to a low volume (3 - 5 mL) on a rotoevaporation system. Then the dialysate is quantitatively transferred to a test tube using several 1 - 2 mL hexane rinses. The dialysate is further reduced, using high purity nitrogen, to ± 0.5 mL.

V. **Gel Permeation Chromatography (GPC)** - For column preparation, calibration, and sample fractionation, see NFCRC SOP: C5.155, "Preparation and Use of Gravity-Flow Gel Permeation Chromatography (GPC) Columns."

VI. **QA/QC** - To verify the integrity of the method and sample handling, the following blanks, spikes and controls are carried through with each set of samples. Usually two (2) samples (see Part III, section 6) are analyzed with the following QA/QC:

1. Process blank - This is a solvent/glassware blank. 250 mL hexane is poured into a dialysis jar and carried through all steps as a sample.
2. SPMD Control - Three (3) 68" SPMDs are filled with ± 2 mL 95% triolein and heat sealed (three [3] seals on each end NFCRC S.O.P.: B5.217, "Preparation of Semipermeable Membrane Devices [SPMDs] with Model Lipid for Monitoring Organic Contaminants in Water"). They are cleaned as described in Part III and dialyzed in 750 mL hexane. They are carried through all steps

described for a sample.

3. Laboratory Recovery Spike - One SPMD from each sample set ((defined earlier) will be used for generating a recovery spike in the following way. (Only one SPMD will be spiked whether or not additional SPMDs are available). After cleaning as in Part III, one end of a membrane is opened and ~ 100,000 cpm (Ca. 1 μg) of 2,2',5,5'-tetrachlorobiphenyl (TCB) is spiked into the SPMD and smoothed along the length of the membrane. Remove excess air and close with three (3) heat seals. Count a like amount of the 2,2',5,5'-TCB using 10 mL Ready Safe^{R} Liquid Scintillation Cocktail (Beckman Instruments, Inc., Fullerton, CA) to verify the amount that was delivered into the SPMD. Using the proper amount of hexane (250 mL hexane for one SPMD or 500 mL for two), dialyze. Before transferring the dialysate to a round bottom flask, measure and count two 5-mL aliquots. (Note: After removing the SPMD from the dialysis jar, rinse the contents of the SPMD into a graduated cylinder, record volume and count two 2 mL aliquots.) Cut the SPMD membrane into small pieces and place the pieces in a counting vial for analysis by liquid scintillation using 10 mL Ready Organic liquid scintillation cocktail (Beckman Instruments, Inc., Fullerton, CA). Reduce the remaining dialysate volume by rotoevaporation and carry through all steps

described for a sample. After processing the spike dialysate through GPC, reduce the "dump" and "collect" fractions to 3 - 5 mL and transfer to counting vials using several 1 - 2 mL hexane washes. Add 10 mL counting cocktail and analyze by liquid scintillation counting.

4. Field Trip or laboratory Blank - Use one to six SPMDs from the appropriate blank sample set, depending on availability and number of samples to be analyzed. Clean as described in Part III and carry through as a sample.

5. The results of all quality control samples are reviewed prior to further sample processing

VII. **Sample fractionation** - Following the completion of the procedure(s) presented above, the sample may be processed further for target analytes using the appropriate class specific enrichment procedure.

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SEMIPERMEABLE MEMBRANE DEVICE (SPMD) CLEANUP AND PREPARATION FOR ANALYSIS

I. **Introduction** - The purpose of this S.O.P. is to delineate key procedural limits of the method yet provide certain specific parameters that currently appear optimal.

II. **Preparation of glassware** - In order to reduce the possibility of the introduction of laboratory contaminants into sample extracts during sample processing or handling, the following procedure is used to clean all glassware:

1. Wash all glassware with laboratory detergent and tap (well water) water. Rinse thoroughly with tap water ($\geq$ 3 times).
2. Rinse each piece of glassware three times with 1 N HCl.
3. Rinse thoroughly with deionized water ($\geq$ 3 times).
4. Rinse three (3) times with acetone (note: all solvents used in the following procedures must be pesticide or nanograde quality, ie. free of contaminants).
5. Rinse three (3) times with hexane.
6. Air dry.
7. Bake in an annealing oven at 475 °C for eight hours.
8. As soon as the glassware is removed from the oven, cover all openings of the glassware with solvent-rinsed (acetone/hexane) aluminum foil and store in drawers or other dust-free areas.
9. Immediately prior to use, rinse each piece of glassware with cyclopentane three (3) times.

Note: Glassware that cannot be annealed, should be rinsed with cyclopentane six (6) times immediately prior to use.

III. **Preparation of SPMDs for dialysis** - When SPMDs are received from field or laboratory exposures, they may have bacteria, algae, sediment, inorganic salts, and other material coating their exterior surface. To prevent this material from

contaminating the dialysate and reducing dialytic recovery, a removal or cleanup step is usually required before dialysis. (Note: Do not touch the SPMD membranes with your hands prior to the following hexane rinse procedure [step 1]). If holes in the SPMDs are visible before cleaning, place dialysis clips on either side of the damaged area and go to step 2. Perform step 1 after heat sealing the damaged SPMD segment.

1. Open the sealed metal or glass container with field deployed SPMDs and pour in ≃ 100 mL hexane. Immediately cover and shake 5 to 10 seconds and then discard the hexane. Care must be used to ensure solvent contact with all SPMD surface. (If the SPMDs are freshly prepared (eg. controls) place in an amber glass jar, add the hexane, shake as above and discard the hexane).

2. Then the SPMDs are placed in a large flat stainless steel pan. Use running tap water (our water is from a deep well and is free of contaminants) and a clean brush and/or hands (ensure gloves or hands are free of soap, powder or oils) to remove all remaining surface material. If the SPMDs have additional seals or loops outside the lipid containment (end) seals, cut them off and discard (this portion of the sampler is usually covered with debris that cannot be easily removed).

3. Drain the water off the SPMDs and swish them in a glass tank containing 1 N HCl for a few seconds (≤ 30 seconds).

4. Thoroughly rinse the SPMDs with tap water to remove the acid.

5. Remove all surface water from the SPMDs, using rinses of acetone followed by isopropanol. Let the rinse solvent evaporate from the SPMDs before dialyzing, by laying the SPMDs on a piece of solvent-rinsed aluminum foil for a few minutes.

Note: Closely inspect the SPMDs for holes as they are cleaned. Water inside the bag is a sure sign of a hole. If there are adequate numbers of undamaged SPMDs, the bad ones can be disposed of. If all are necessary for a sample, make 2 heat seals on either side of the hole. Use the SPMDs as usual but note which ones were damaged.

IV. Dialysis - Canning jars, 1 and 2 quart size, with solvent-rinsed aluminum foil under the screw type lids to create a tight seal are used for the dialysis step. The amount of hexane used for dialysis depends on the total mass of membrane and lipid. A 68" SPMD filled with ≃ 2 mL lipid, requires 250 mL hexane, thus 2 bags require 500 mL, etc. Dialyze the SPMDs at a constant 18 °C for 48 hours. After 48 hours, the membranes are removed from the jar and usually discarded following proper disposal procedures. The dialysate is

quantitatively transferred (using three 3 to 5 mL rinses of hexane) into a round bottom flask equipped with a rotary evaporator trap and reduced to a low volume (3 - 5 mL) on a rotoevaporation system. Then the dialysate is quantitatively transferred to a test tube using several 1 - 2 mL hexane rinses. The dialysate is further reduced to ≃ 1 mL, using high purity nitrogen.

V. **Filtration** - A filtration step is necessary to remove particulates from the extracts before further processing.

1. Poke a little piece of glass fiber filter in a disposable pipet. Pre rinse this "column" with a mixture of 80/20 (v/v) hexane/methylene chloride.

2. Filter the ≃ 1 mL sample through the prepared column.

3. Rinse the tube using several 1 to 2 mL washes of 80/20 and filtering these washes through the column.

4. Rinse the filter with an additional 1 mL of 80/20.

5. Evaporate to 5 mL.

6. Rinse the filter thoroughly between samples.

VI. **Lipid determination** - A lipid analysis can be done on selected dialysates to determine the amount of lipid and/or polyethylene waxes in the samples. Choose at least one sample from each field site plus a control for a lipid analysis. Bring the selected samples to exactly 5 mL. Remove one tenth of the sample (500 μL) and place in a preweighed shell vial. After all the solvent has evaporated, reweigh the vial. By multiplying by 10, the total waxes and lipid per sample can be calculated and the proper GPC method to be used can be determined. If the amount of lipid determined in this step is > 10% of the original lipid mass in the SPMD, a small hole (s) in the membrane is indicated. (Note which samples have had a tenth removed)

VII. **Gel Permeation Chromatography (GPC)** - GPC has proven to be a necessary cleanup step for all SPMD dialysates regardless of which classes of contaminants are targeted for analysis. This is because it is the only innocuous cleanup technique that can remove co-dialyzed lipids and polyethylene waxes.

1. <u>Instrumentation</u>: The GPC instrument consists of the following modular components. 1) Perkin-Elmer Series 410 Solvent Delivery System (pump); 2) Perkin-Elmer ISS-200 Sample Handling System (autoinjector); and 3) Isco Foxy 200 fraction collector. For purposes of calibrating the GPC separation, a UV absorbance detector (254 nm) and strip chart recorder are also used.

2. Columns: There are three options as to which column or columns will be used; the only differences between the columns is their size. The choice will be made by the chemist operating the GPC, and his decision will be based upon the results of the percent lipid analysis. 1) 22.5 mm id X 250 mm column; 2) 7.8 mm id X 600 mm column; or 3) two 7.8 mm id X 600 mm columns in tandem. All of the columns described above contain 10 μm particle size, 10 nm pore size Phenogel. All columns are used in series with the prescribed Phenomenex precolumn.

3. Mobile Phase: 80/20; hexane-dichloromethane (V+V)) pumped at 4.0 mL/min for the wider bore column, or 3.0 mL/ min for the narrower bore columns.

4. GPC Calibration: The chromatographic separation is calibrated by injection of 100 μL of a solution containing DEHP, benzene, biphenyl, sulfur, and pyrene. These materials elute in the sequence in which they were listed. The chromatogram is examined and compared to previously generated calibration chromatograms. If all peaks and separations between peaks appear normal, the retention time of the benzene is measured and recorded. The benzene peak is the basis upon which the retention time that is the end of the dump fraction and the beginning of the collect fraction is chosen. The cutoff point is chosen in such a way that it is as late as possible with the entire benzene peak still being in the collect fraction. The absolute retention times and volumes for the benzene will vary greatly depending upon which GPC column is chosen. Regardless of the column, the end of the dump fraction should be chosen as described. The end of the collected fraction should be chosen in such a way that the total collected fraction is 3.33-times as long as the dump fraction.

5. Sample Preparation: The samples (as prepared in steps V and VI) will be reduced in volume to less than 1 mL under gentle streams of nitrogen. Then CH_2Cl_2 will be used to transfer the samples to conical, 1-mL autoinjector vials. After an entire sample has been quantitatively transferred, a nonane keeper is added to the vial, and most of the CH_2Cl_2 is evaporated away. Then the solution volumes are adjusted to 0.95 mL by the addition of nonane. (So as to ensure that the entire sample is injected, we will program the autoinjector to inject 1.00 mL. It will inject the sample plus 0.05 mL of air.)

6. In accordance with the Perkin-Elmer HPLC and autoinjector operators manuals and the Isco Foxy fraction collector manual, program the modular GPC apparatus to perform the separation in accordance with the results of the calibration chromatogram. Collect the desired fractions on the fraction collector platform in 125 or 250-mL

NFCRC Protocol: 92-33-02
Work Unit No.: 30063

Date Prepared: May 6, 1992

Date Revised:

Study 92-33-02: Assessment of Missouri River Habitat Quality with Semipermeable Membrane Devices (SPMDs)

This research will be conducted in general accordance with National Fisheries Contaminant Research Center's Quality Assurance guidelines (appropriate sections from: 160.120, 40 CFR Ch.1, 7-1-85, subpart G- "Protocol for and conduct of a study").

This Protocol addresses the research presented in NFCRC Work Unit 30063.

TABLE OF CONTENTS:

1. Title and Purpose of Study

Title of Study: Assessment of Missouri River Habitat Quality with Semipermeable Membrane Devices (SPMDs).

Purpose of Study: The purpose of this study is to demonstrate the use of SPMDs as a screening tool for the assessment of selected hydrophobic organic contaminants in the Missouri River System and to provide a relative ranking of the various demonstration sites in regards to the presence of these contaminant residues.

2. Identification of Test and Control Substances

There are no animals associated with this study. However, for the purposes of this protocol, the test and control substances are defined

as those contaminant residues [polyaromatic hydrocarbons (PAHs), organochlorine pesticides (OCs), polycholorinated biphenyls (PCBs)] sequestered in the SPMDs during the exposure period.

3. Name and Address of Sponsor and Testing Facility

Sponsor: U.S. Fish and Wildlife Service, Department of the Interior
Washington, D.C.

Testing Facility: National Fisheries Contaminant Research Center (NFCRC)
4200 New Haven Road, Columbia, Missouri 65201

4. Proposed Starting and Completion Dates

June 8, 1992 to July 31, 1993

5. Justification for Selection of the Test System

Successful restoration of fisheries and wetlands in the Missouri River Basin will require a comprehensive assessment of environmental contaminant issues. Contaminants such as chlordane and PCBs have led to consumption advisories on sturgeon, paddlefish and catfish, seriously diminishing the aesthetic, recreational, and commercial value of a multi-million dollar fishery. Further, organochlorine residues from past insecticidal usage have been implicated in mortalities of endangered species of bats and shorebirds.

Traditional methods of contaminant assessment such as residue analysis of fish, sediments, or water can be costly. Moreover, such data can be difficult to obtain and interpret due to insufficient detection limits, analytical interferences, hydrological variation, contaminant metabolism, and sentinel organism movement and availability.

The SPMD technology offers an innovative alternative to traditional contaminant assessment methods. Hydrophobic organic contaminants sequested in the SPMDs represent a time-weighted average residue level (up to the theoretical equilibrium limit). No metabolic activity occurs ensuring that those contaminants (e.g. PAHs) that are rapidly metabolized by sentinel organisms will be accumulated by the SPMDs. Consequently, the sequestered residues can be analyzed by any of a variety of techniques.

The SPMDs will be prepared as described in NFCRC SOP B5.217 (latest revision). These devices consist of 152.cm length of 2.54 cm wide layflat virgin polyethylene tubing (Brentwood Plastics, Brentwood, MO). Each SPMD will contain 1.82 g of 95% triolein and will be heat sealed at each end of the tube. Prior to use, the tubing will be extracted and the triolein checked for interfering substances and dialyzed if necessary, as described in NFCRC SOP B5.217.

6. Species Number, Body Weigh, Sex and Source

Not applicable, no animals used in study.

7. Procedure for Identification of Test Systems

Not applicable, no animals used in study.

8. Experimental Design

The general methodology to be used in this study includes investigations into the optimum processing of SPMDs regarding reduction in biofouling, contamination from air-borne pollutants, residue enrichment techniques and field deployment. The SPMD technique will be used to determine the relative amounts of hydrophobic organic contaminants in various reaches of the Missouri River. Specifically, SPMDs will be placed in the main stem of the Missouri River at five locations. These five locations; Sioux City, IA, Nebraska City, IA, Kansas City, MO, Glasgow, MO and Herman, MO are located in proximity to large tributary streams. The SPMDs will be placed approximately 0.5 miles downstream and on the opposite bank from the confluence of the tributary stream with the Missouri River. Four replicate SPMDs will be deployed at each of the five demonstration sites; resulting in a total of twenty samples. For the purposes of this study, a sample will consist of two ,1.82 g SPMDs (3:64 g total triolein) per composite.

Sampler arrays will consist of SPMDs mounted on the inside of stainless steel mesh cages (25 cm X 25 cm X 91 cm length) suspended approximately 1.0 m below the surface of the water. Each cage will contain eight SPMDs. Two cages will be deployed at each of the five demonstration sites. Average water temperature will be determined using a TempMentor® (Ryan Instruments, Redmond, WA). The SPMDs will be deployed as outlined in NFCRC F4.1 (latest revision).

All SPMDs will be transported (to and from sites) sealed in precleaned steel paint cans. Following a 28 day exposure, the SPMDs will be recovered and transported to the NFCRC for further processing. SPMD processing and sample enrichment techniques will follow the latest revisions of current NFCRC Chemistry SOPS (C5.173; C5.155; C5.66; C5.68; C5.144). Analytical determinations will be conducted using capillary gas chromatography with electron capture and photoionization detection. As appropriate, selected samples will be examined for unknowns and for confirmation of tentatively identified contaminants, using gas chromatography/mass spectrometry.

Blank SPMDs will be accompany the sampler arrays deployed at the five demonstration sites. These blanks will consist of day zero and day 28 blanks and will be treated in an identical manner to the exposure samples. Upon arrival at NFCRC all SPMDs will be stored at -20°C until processing is initiated.

9. Diet and Solvents

No animals will be used in the study, consequently, diets are not applicable. Solvents used in SPMD processing and sample enrichment procedures are provided in the appropriate NFCRC SOP. All solvents used are of nonograde or higher purity.

10. Route of Administration

Not applicable, no animals used in study.

11. Dosage Levels of Control Substances

Not applicable, no animals used in study.

12. Method to Measure Degree of Test Substances Adsorption

SPMDs will be transported to NFCRC and will be processed according to NFCRC SOP C5.173 (latest revision). The resulting dialysates will be enriched and analyzed (NFCRC SOP's C5.155; C5.66; C5.68; C5.144 - latest revisions) for the following organic residues:

A. NCBP Organochlorines and PCB's

Hexachlorobenzene (HCB)	o,p'-DDE
Pentachloroanisole (PCA)	p,p'-DDE
α-BHC	Dieldrin
Lindane	o,p'-DDD
β-BHC	Endrin
Heptachlor	Cis-nonachlor
δ-BHC	o,p'-DDT
Aldrin	o,p'-DDD
Dacthal	o,p'-DDT
Oxychlordane	Mirex
Heptachlor Epoxide	Toxaphene
Trans-chlordane	1248
Trans-nonachlor	1254
Cis-Chlordane	1260

B. Priority Pollutant PAHs

Acenaphthene
Acenaphthylene
Anthracene
Benz(a)anthracene
Benzo(b)fluoranthene
Benzo(k)pyrene
Chrysene
Dibenz(a,h)anthracene
Flouranthene
Flourene
Indeno(1,2,3-c,d)pyrene
Naphthalene
Phenanthrene

Following determination of the contaminant residues sequestered in the SPMDs, the data will be related to the average water temperature at each demonstration site during the period of exposure. This correction will allow a comparison of the amount of residues sequestered at each demonstration site. Analysis of the residue data (i.e. presence, means, etc.) will provide the basis of a relative contaminant ranking. This

relative ranking provides information concerning the severity of hydrophobic organic contamination at each demonstration site in the Missouri River.

13. Type and Frequency of Tests, Analyses, and Measurements

Water temperature will be recorded hourly (TempMentor®, Ryan Instruments, Redmond, WA). Operation and calibration instructions for the TempMentor are presented in the literature and software supplied by the manufacturer. Analyses of contaminant residues will be initiated following SPMD processing and contaminant enrichment.

14. Records

All raw data, data summaries, and analytical data will conform to the NFCRC Quality Assurance Guidelines.

15. Date of Approval of Study Plan

Prepared by:

J.D. Petty
Senior Research Scientist
Principle Investigator

5/12/92
Date

Approved by:

Ted R. Schwartz
Chief, Chemistry Division

5/13/92
Date

Joseph B. Hunn
Quality Assurance Officer

5-18-92
Date

Richard A. Schoettger
Center Director

5-18-92
Date

16. Statistical Analysis

The experimental data obtained from this study will be analyzed by standard statistical techniques and will be used to prepare a relative index of contamination. If an examination of the data (i.e. chromatograms, reconstructed ion chromatograms, etc.) indicates the presence of concentration independent factors, the data may be analyzed using multivariant techniques (i.e. principal components analysis).

ORGANOCHLORINE DETECTION and QUANTITATION LIMITS – MDLs and MQLs

NANOGRAMS per SAMPLE (2 SPMDs per Sample)

sample name:	Reagent Blank #1	Reagent Blank #2	Reagent Blank #3	Reagent Blank #4	Reagent Blank #5	Reagent Blank #6	AVG RegBlnk	Std Dev	MDL*	MQL*
HCB	0.5	0.1	2.0	1.6	0.3	2.6	1.2	0.9	4.0	10.6
PCA	0.1	0.9	0.5	0.2	0.2	0.2	0.4	0.3	1.2	3.1
ALPHA BHC	0.0	0.0	0.0	0.0	0.0	0.3	0.1	0.1	0.4	1.2
LINDANE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
BETA BHC	0.0	1.1	0.0	0.0	0.0	0.0	0.2	0.4	1.4	4.3
HEPTACHLOR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DELTA BHC	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DACTHAL	1.8	2.9	1.8	2.2	1.1	4.4	2.4	1.1	5.5	12.9
OXYCHLORDANE	0.0	0.0	0.0	0.0	0.3	0.0	0.1	0.1	0.4	1.2
HEPTACHLR EPOX	0.5	0.0	0.0	0.0	0.6	0.3	0.2	0.2	1.0	2.7
T–CHLORDANE	0.0	0.0	0.5	0.0	0.6	0.6	0.3	0.3	1.1	3.1
T–NONACHLOR	1.5	0.9	0.9	0.0	0.4	0.8	0.8	0.5	2.1	5.4
C–CHLORDANE	3.8	3.0	2.2	0.5	0.3	2.6	2.1	1.3	5.9	14.8
o,p'–DDE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DIELDRIN	0.9	2.0	2.8	0.8	0.0	0.7	1.2	0.9	4.0	10.5
p,p'–DDE	1.1	0.4	1.6	0.6	0.0	0.6	0.7	0.5	2.3	5.8
o,p'–DDD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ENDRIN	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C–NONACHLOR	0.0	0.3	0.0	0.3	0.0	0.0	0.1	0.1	0.5	1.5
o,p'–DDT	0.0	0.9	3.9	0.0	0.0	0.9	1.0	1.4	5.1	14.7
p,p'–DDD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
p,p'–DDT	1.4	0.0	0.0	0.0	0.0	0.0	0.2	0.5	1.8	5.5
MIREX	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
METHOXYCHLOR	0.0	0.0	0.0	5.0	0.0	0.0	0.8	1.9	6.4	19.5

* MDL = (AVG RegBlnk) + 3(Std Dev)
MQL = (AVG RegBlnk) + 10(Std Dev)

SUMMARY of ORGANOCHLORINE METHOD SPIKE RECOVERIES
N = 7

	Average	Coef.Var.
HCB	74	9
PCA	72	11
ALPHA BHC	74	17
LINDANE	76	10
BETA BHC	82	10
HEPTACHLOR	60	14
DELTA BHC	84	15
DACTHAL	96	15
OXYCHLORDANE	82	9
HEPTACHLOR EPOXIDE	85	9
T-CHLORDANE	66	14
T-NONACHLOR	84	19
C-CHLORDANE	89	11
o,p'-DDE	86	16
DIELDRIN	84	12
p,p'-DDE	82	14
o,p'-DDD	103	14
ENDRIN	84	11
C-NONACHLOR	95	15
o,p'-DDT	62	16
p,p'-DDD	87	16
p,p'-DDT	70	22
MIREX	85	14
METHOXYCHLOR	76	21

DETECTION LIMITS and SPIKE RECOVERY – MISSOURI RIVER SPMDs

SAMPLE	TOTAL TOXAPHENE – NG / SAMPLE			percent recovery
	Process Blanks	Field blanks	SPMD Blanks	REAGENT SPIKES
1	17	49	81	76
2	23	21	35	70
3	41	51	90	69
4	4	45	79	67
5	11	64	95	72
6	21	9	15	
7	13	11	52	
8		21		
9		13		
average (corrected)	19	32	64	71
std.dev.	12	21	30	3
range	4–41	9–64	15–90	67–76
Toxaphene / sample	**19**	**32**	**64**	**71% average**

MDL = AVG. Reag Blank + 3(Std.Dev.) = 50 ng/ sample

18.5 + 3(11.8) = 50

DETECTION LIMITS and SPIKE RECOVERY – MISSOURI RIVER SPMDs

SAMPLE	TOTAL PCBs – NG / SAMPLE			percent recovery
	Process Blanks	Field blanks	SPMD Blanks	REAGENT SPIKES
1	43	1390	718	85
2	27	190	171	82
3	45	86	177	63
4	208	116	205	86
5	40	393	337	89
6	45	190	147	
7		131	175	
8		101		
9		170		
10		130		
average	68	290	276	81
std.dev.	101	137	74	10
range	40–208	86–1390	147–718	63–89
PCB total / sample	**70**	**290**	**280**	**81% average**

MDL = AVG. Reag Blank + 3(Std.Dev.) = 350 ng/ sample
= 200 + 3(50) = 350

PAH DETERMINATION – MISSOURI RIVER SPMD PROJECT

UG/ SAMPLE **PAH DETECTION LIMIT CALCULATIONS**

	REAGENT BLANKS, PROCESS BLANKS, SPMD LAB BLANKS						
	BLANKs SET #1	BLANKs SET #2	BLANKs SET #3	BLANKs SET #4	BLANKs SET #5	BLANKs SET #6	BLANKs SET #7
naphthalene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
acenaphthalene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
acenaphthene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
fluorene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
phenanthrene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
anthracene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
fluoranthene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
pyrene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
benz(a)anthracene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
chrysene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
benzo(b)fluoranthene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
benzo(k)fluoranthene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
benzo(a)pyrene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
indeno(123cd)pyrene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
dibenz(ah)anthracene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
benzo(ghi)perylene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

MDL = AVERAGE BLANK + 3 (STD. DEV.*) = 0.10 UG / SAMPLE

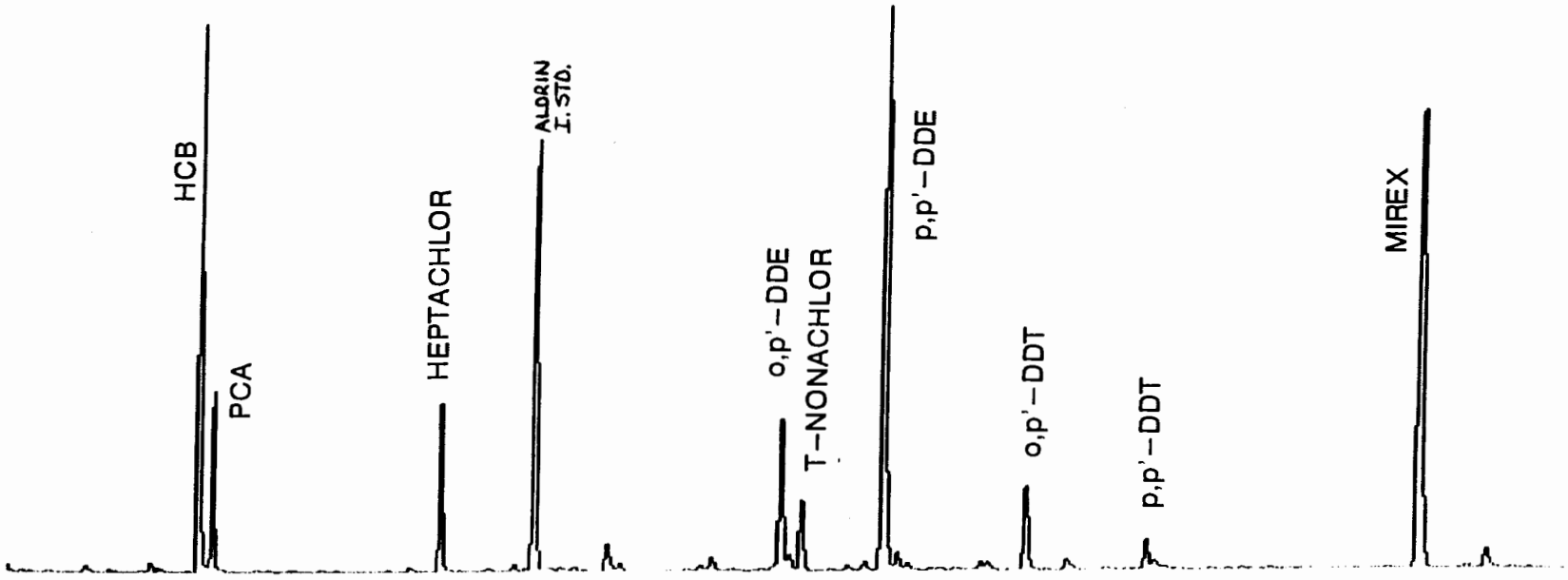
= 0.05 + 3(0.015) = 0.095

* (Std. Dev. from spike analyses)

SUMMARY of P A H METHOD SPIKE RECOVERIES N = 7		
Priority Pollutant PAHs	Average % Recovery	Coef.Var.
naphthalene	82	13
acenaphthalene	83	13
acenaphthene	86	14
fluorene	88	14
phenanthrene	87	13
anthracene	89	12
fluoranthene	88	14
pyrene	86	14
benz(a)anthracene	94	12
chrysene	93	12
benzo(b)fluoranthene	90	14
benzo(k)fluoranthene	92	14
benzo(a)pyrene	90	13
indeno(123cd)pyrene	88	13
dibenz(ah)anthracene	87	14
benzo(ghi)perylene	82	15

REAGENT SPIKE- OC Pesticides
SG-1 Fraction

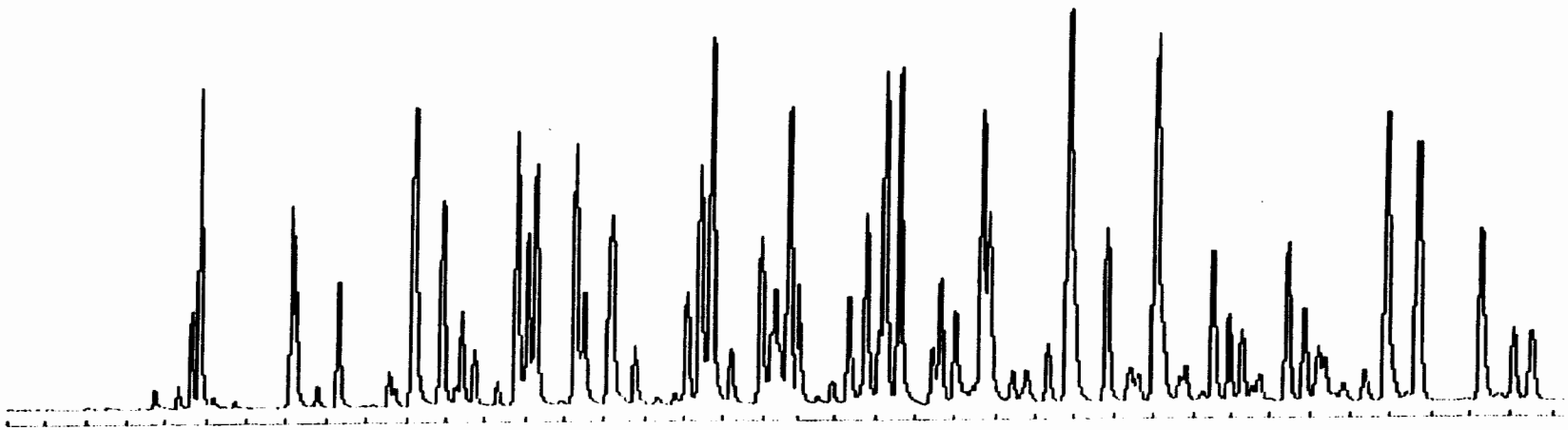
GC-ECD (DB5)
Scale 50



TIME 10.00

REAGENT SPIKE- PCBs
SG-1 Fraction

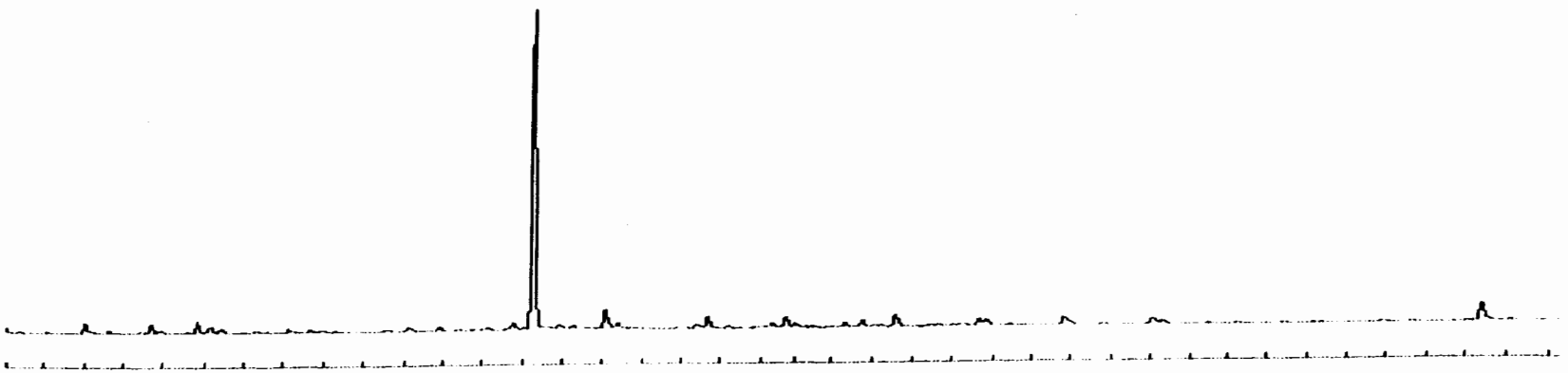
GC-ECD (DB5)
Scale 150



TIME 10.00

REAGENT BLANK
SG-1 Fraction

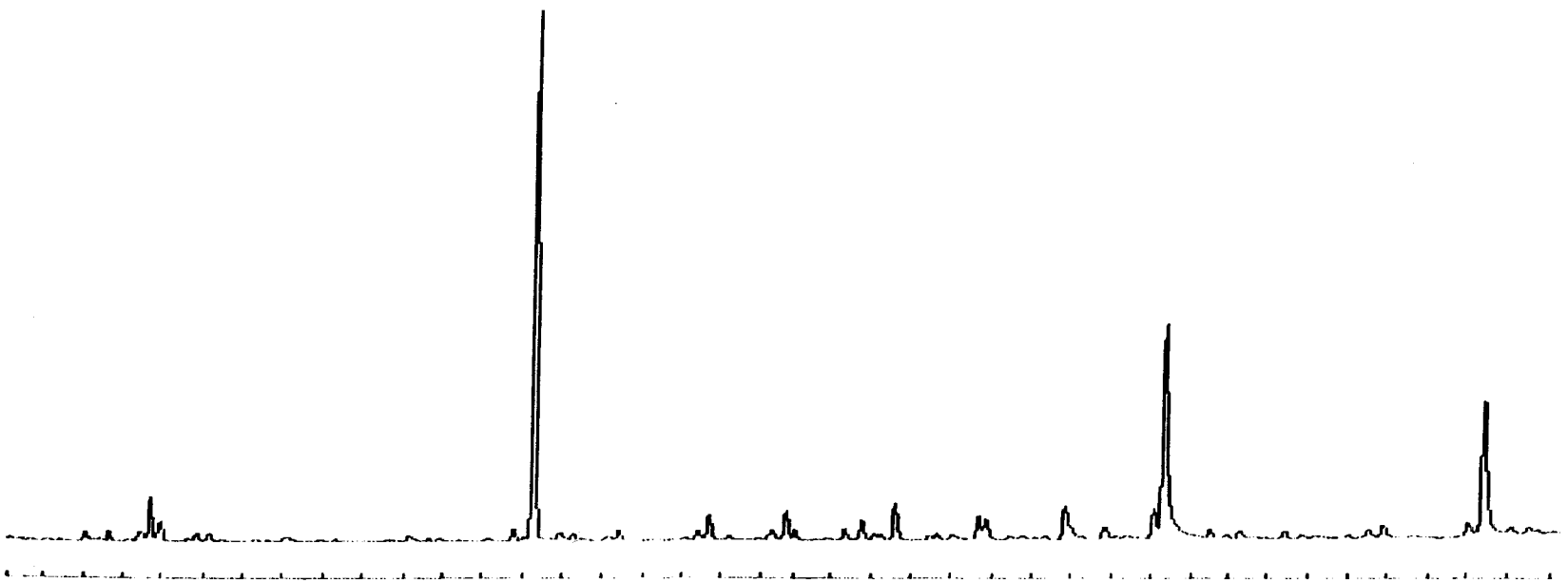
GC-ECD (DB5)
Scale 50



TIME 10.00

PROCESS BLANK
SG-1 Fraction

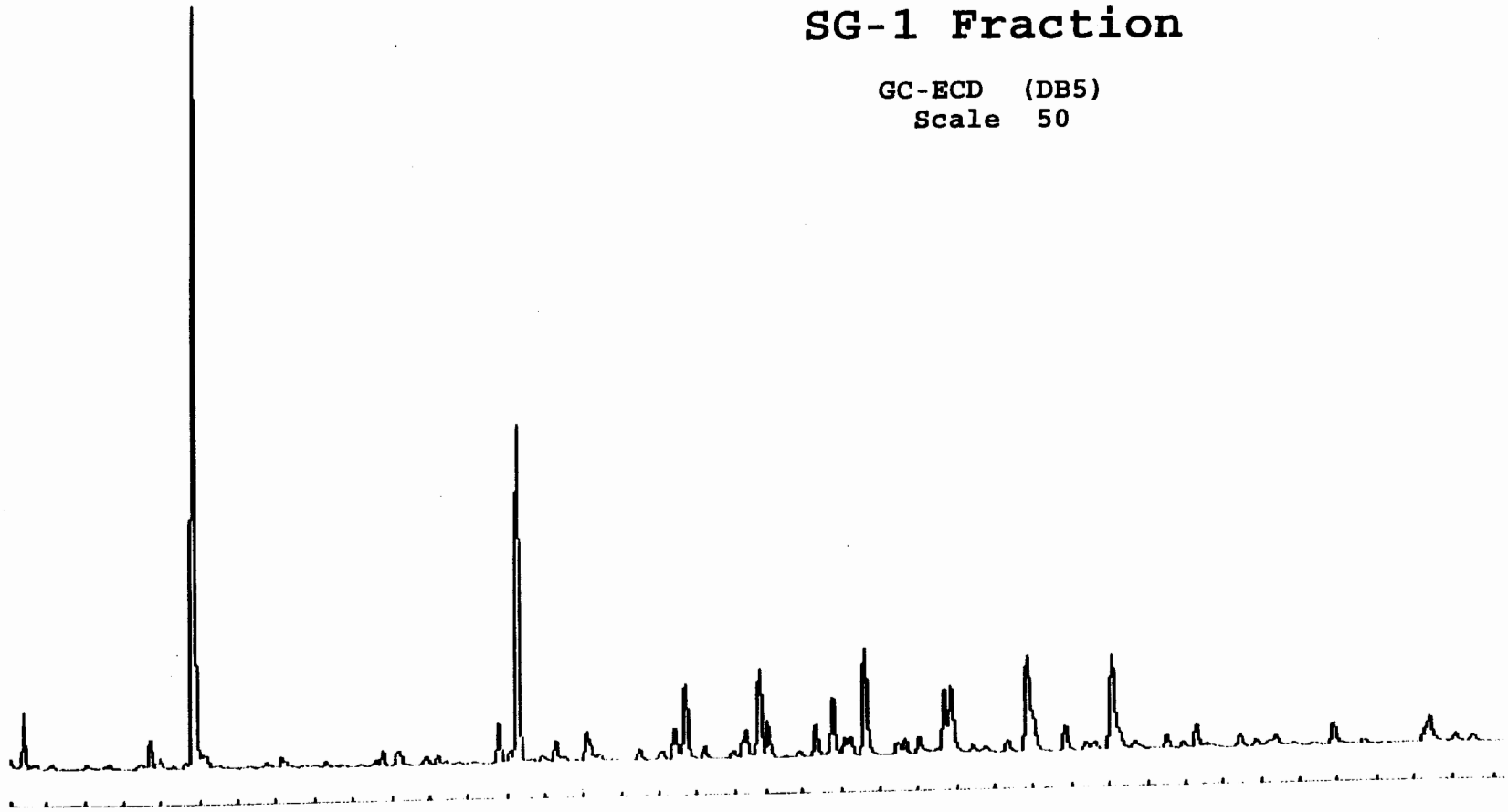
GC-ECD (DB5)
Scale 50



TIME 10.00

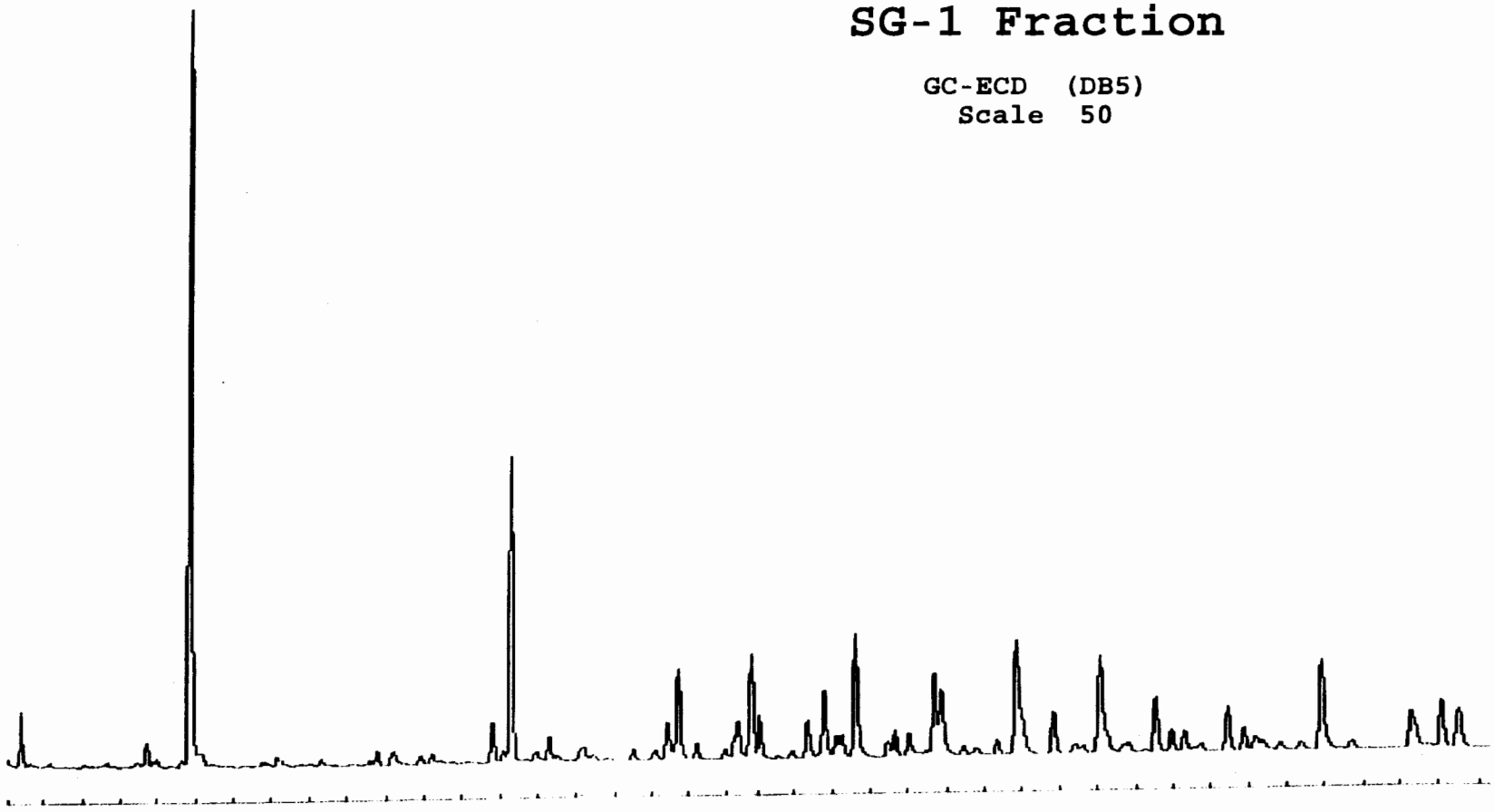
SPMD LAB BLANK
SG-1 Fraction

GC-ECD (DB5)
Scale 50



FIELD BLANK- DAY 0
SG-1 Fraction

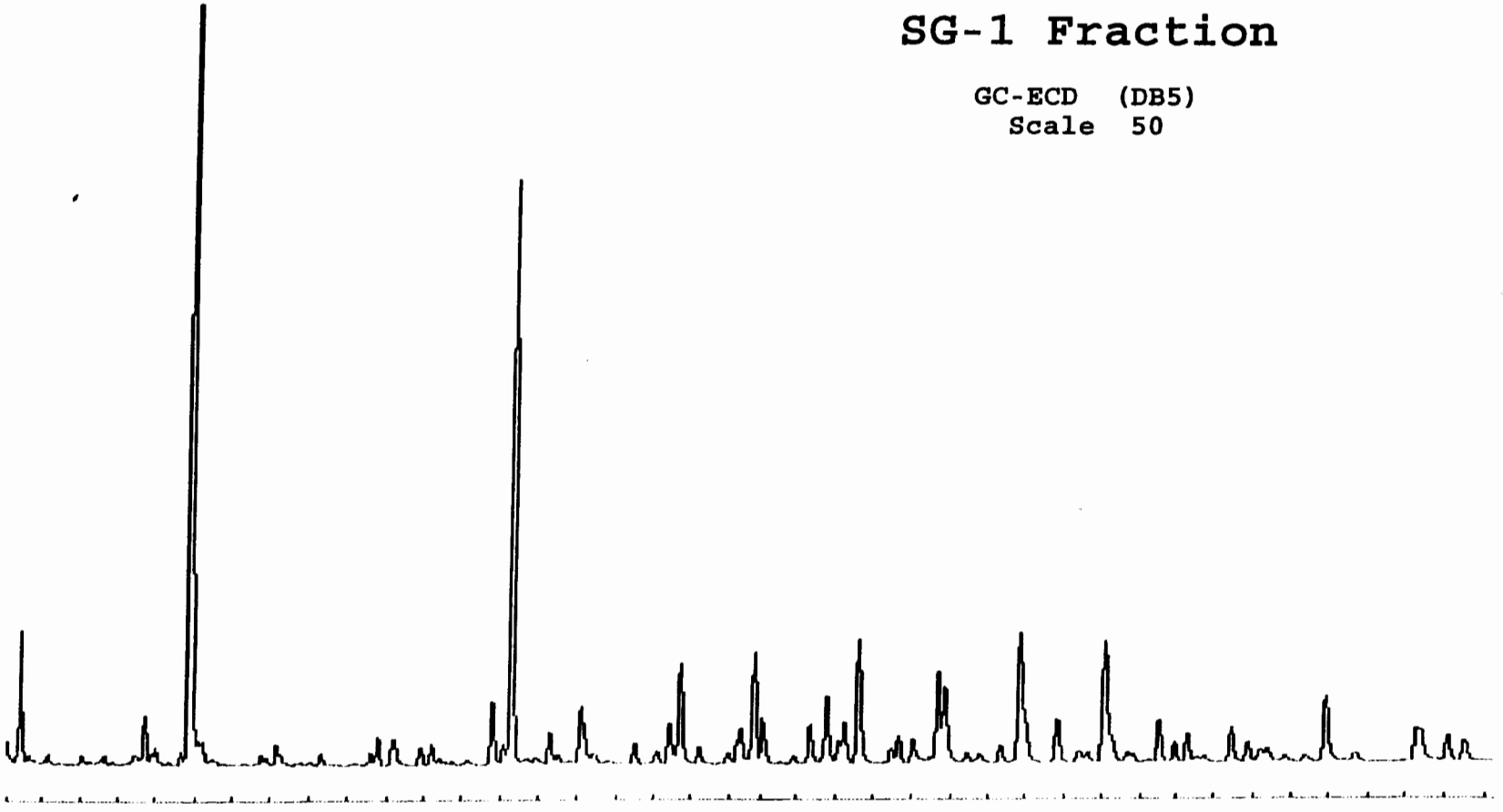
GC-ECD (DB5)
Scale 50



WE 10.00

FIELD BLANK- DAY 28
SG-1 Fraction

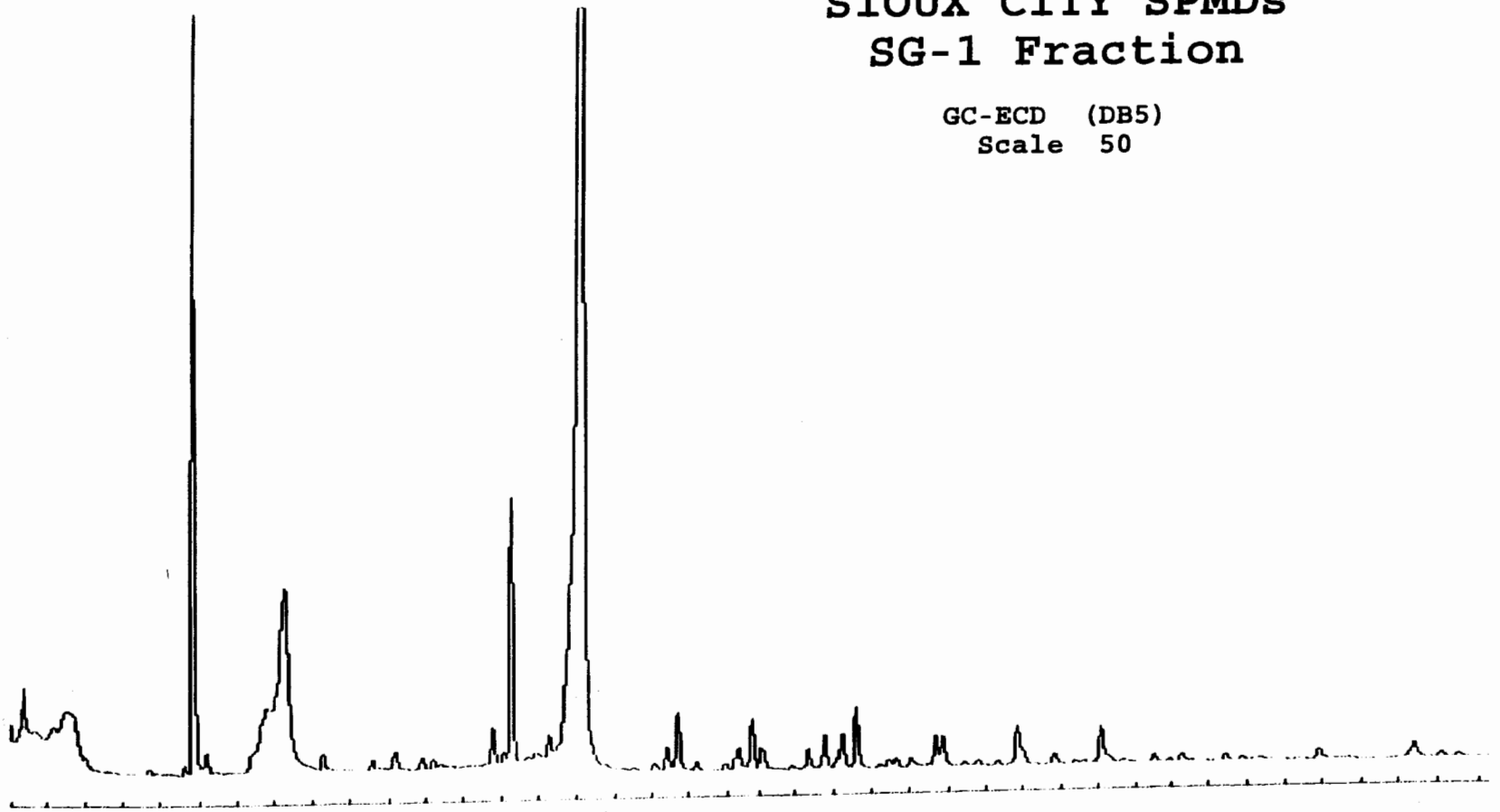
GC-ECD (DB5)
Scale 50



TIME 10.00

SIOUX CITY SPMDs
SG-1 Fraction

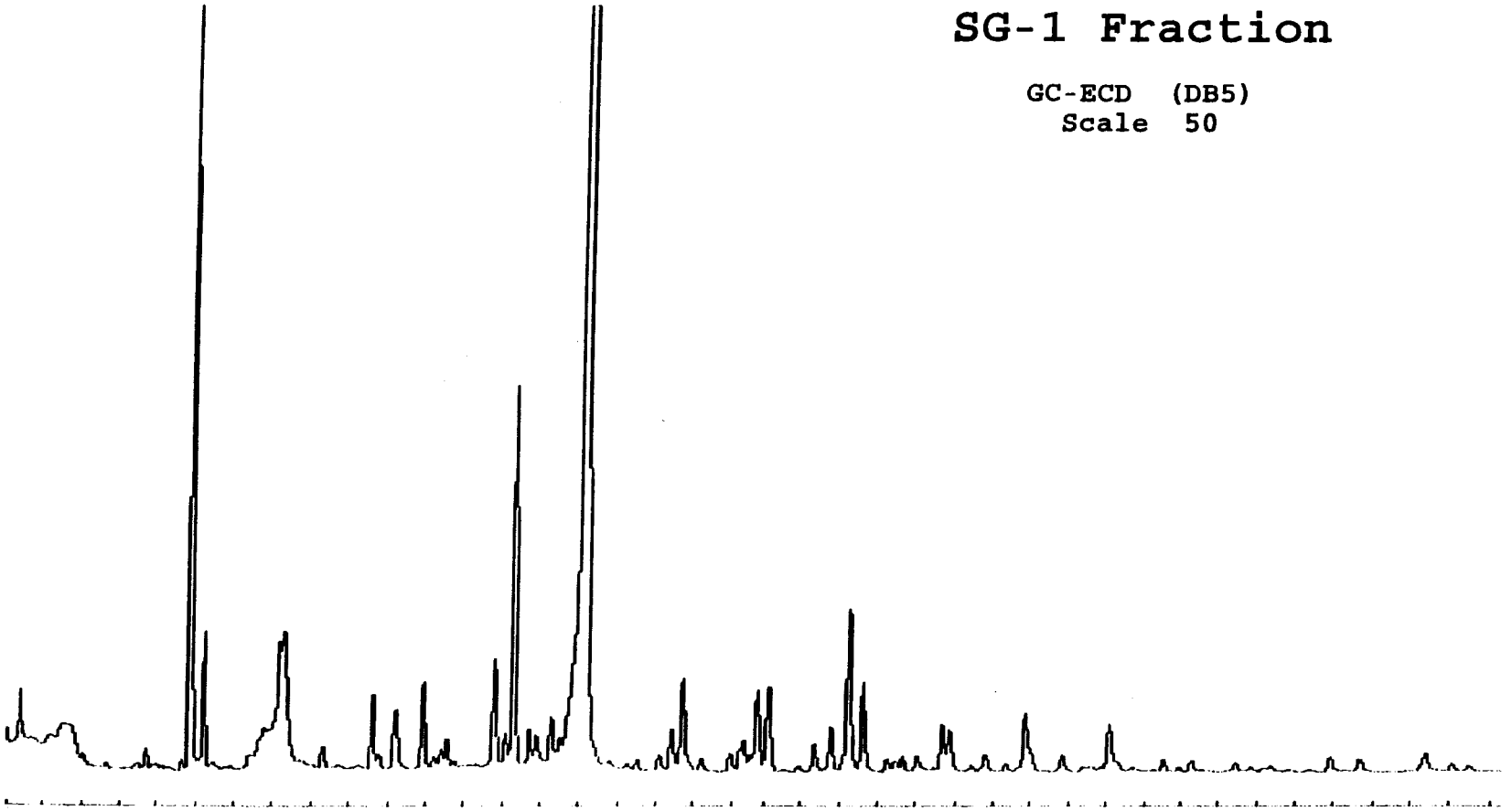
GC-ECD (DB5)
Scale 50



ME 10.00

NEBRASKA CITY SPMDs
SG-1 Fraction

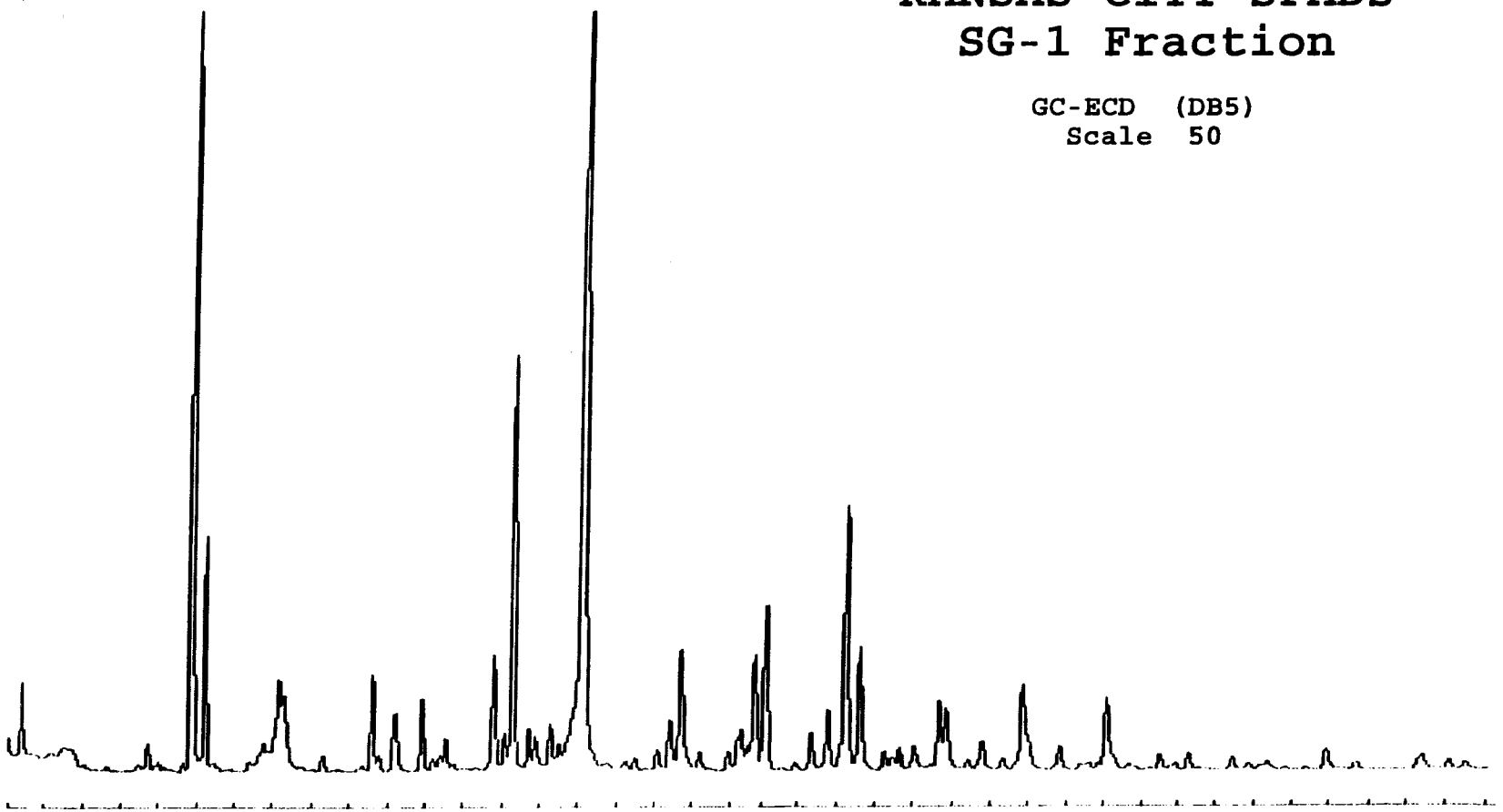
GC-ECD (DB5)
Scale 50



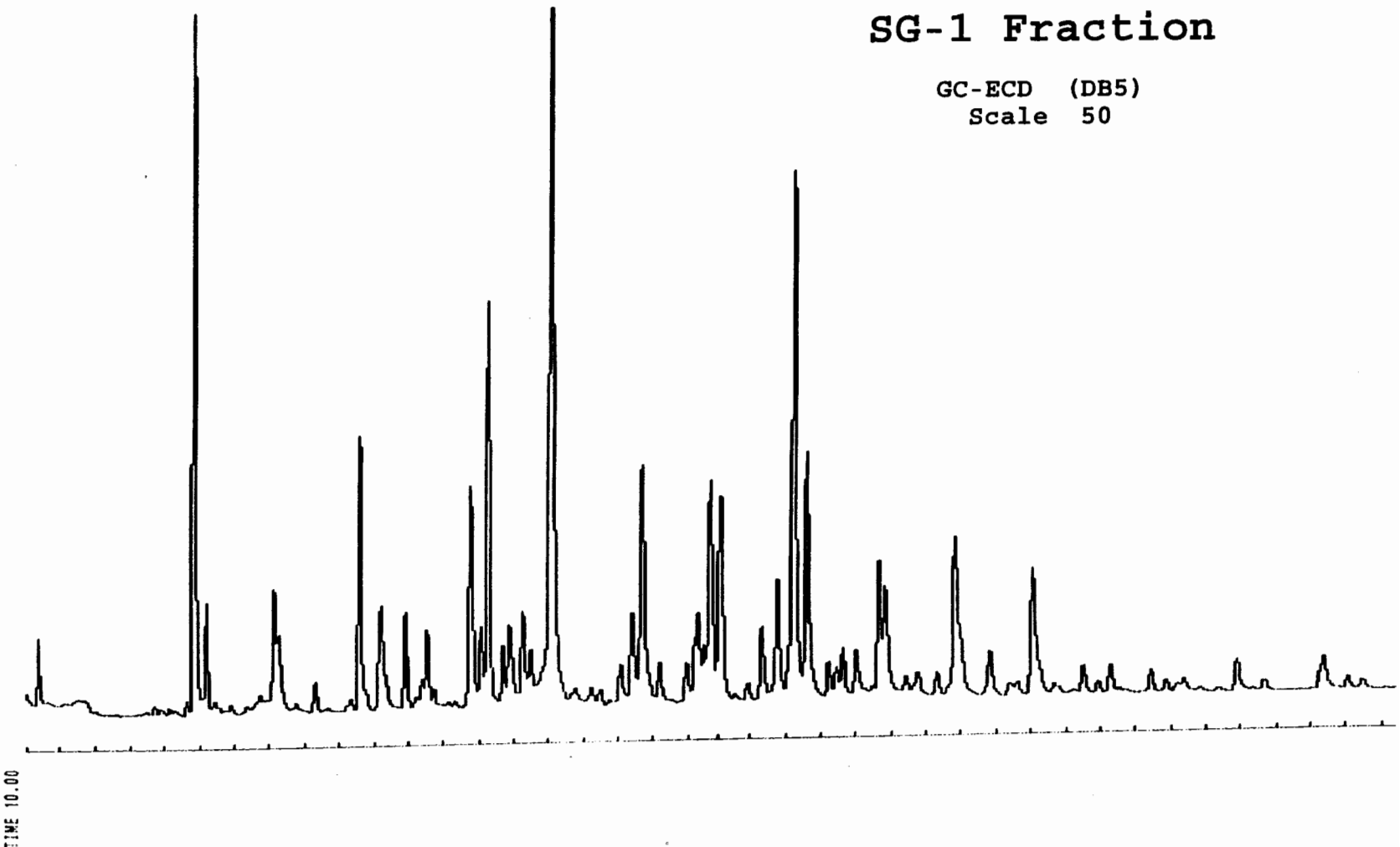
WE 10.00

KANSAS CITY SPMDs
SG-1 Fraction

GC-ECD (DB5)
Scale 50

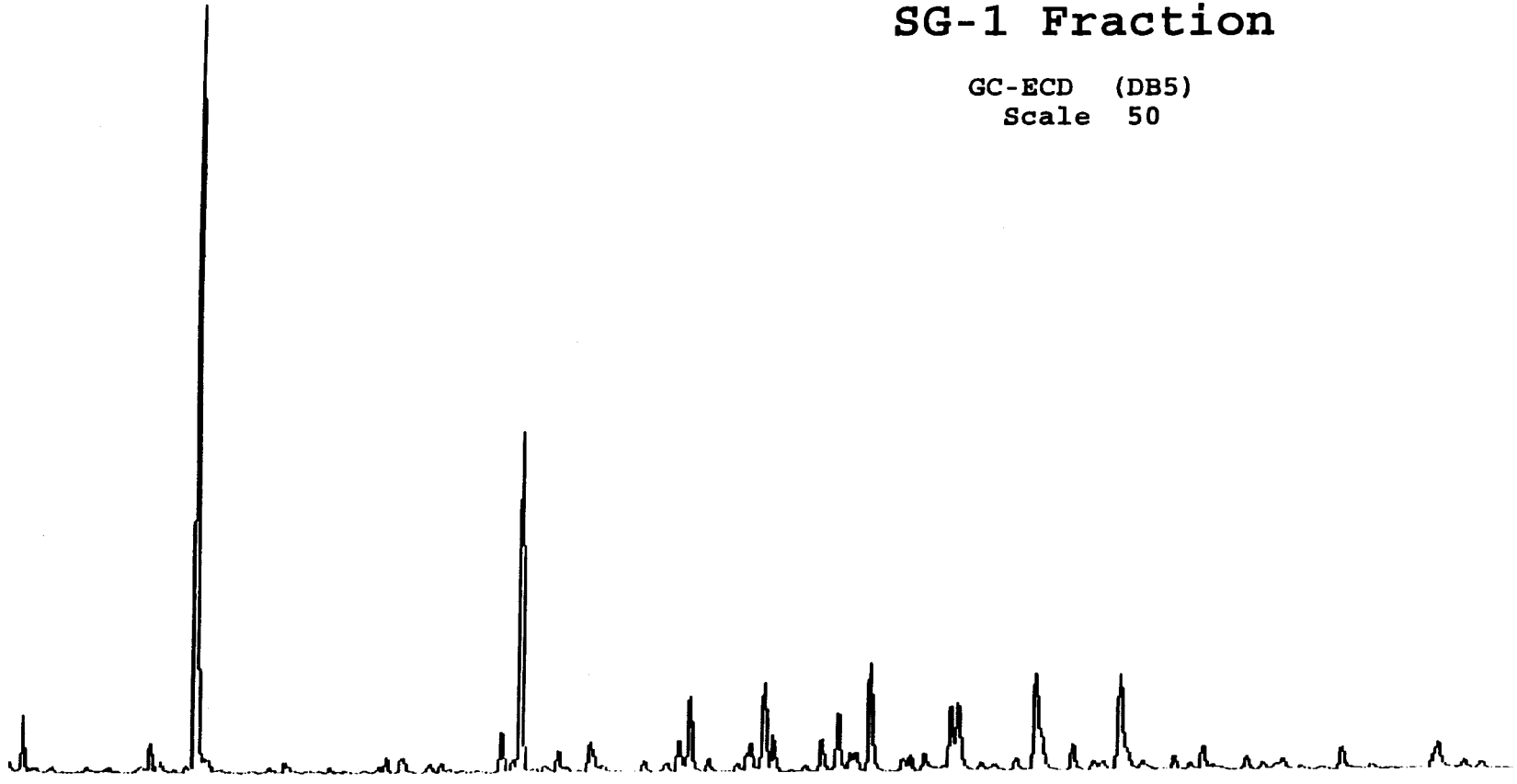


TIME 10.00


GLASGOW SPMDs
SG-1 Fraction
GC-ECD (DB5)
Scale 50
TIME 10.00

HERMANN SPMDs
SG-1 Fraction

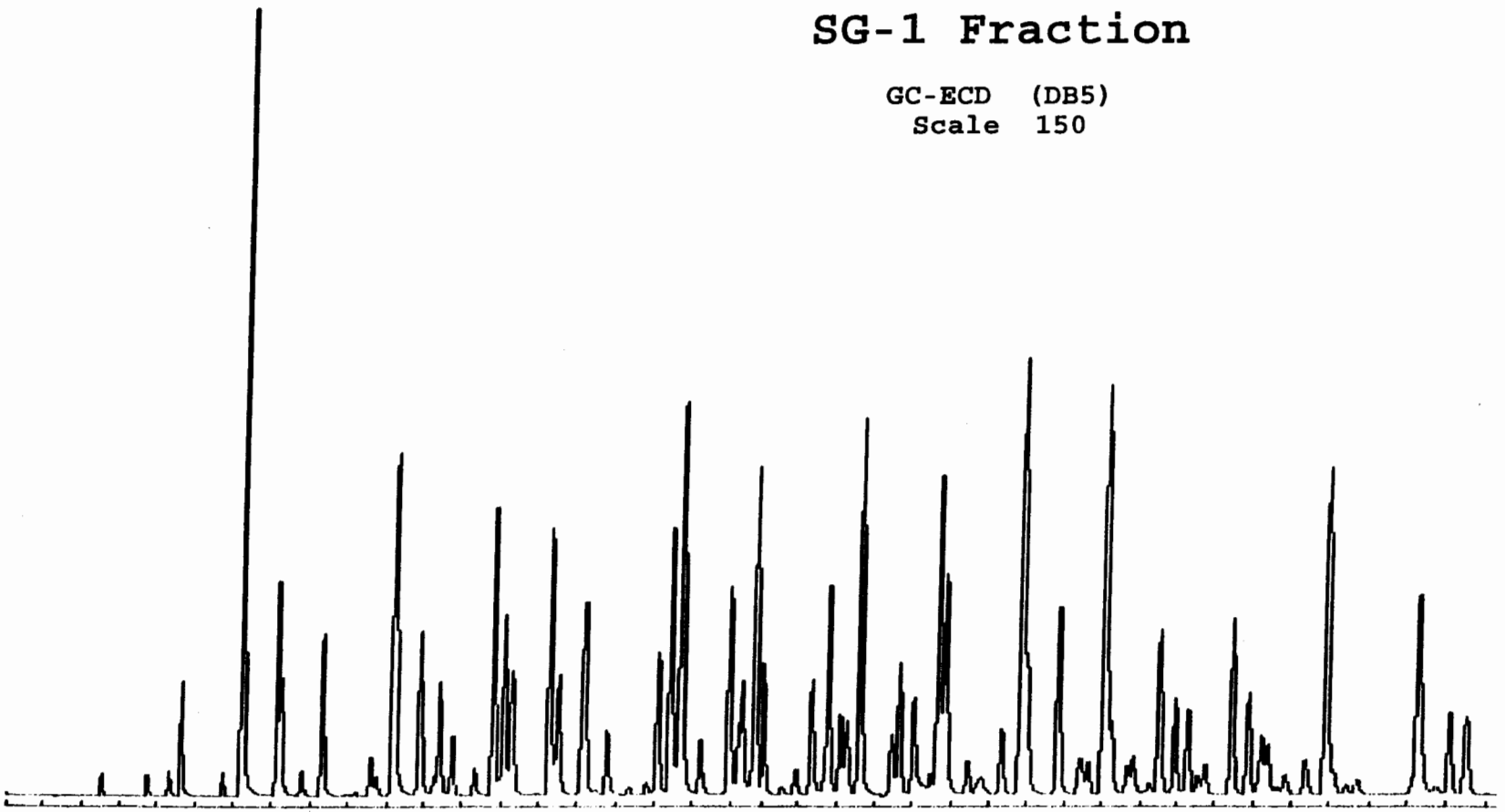
GC-ECD (DB5)
Scale 50



TIME 10.00

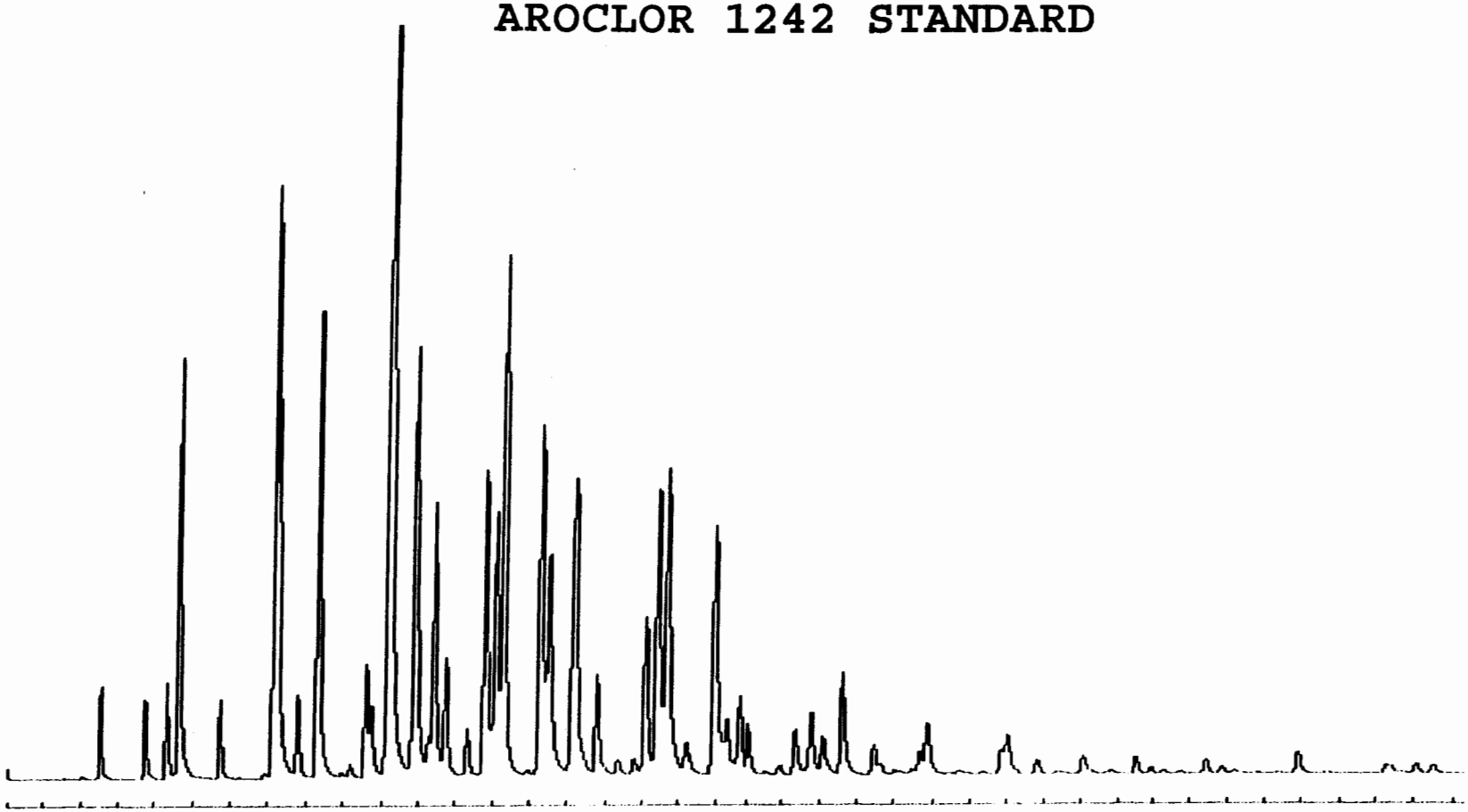
PCB A-1111 STANDARD
SG-1 Fraction

GC-ECD (DB5)
Scale 150



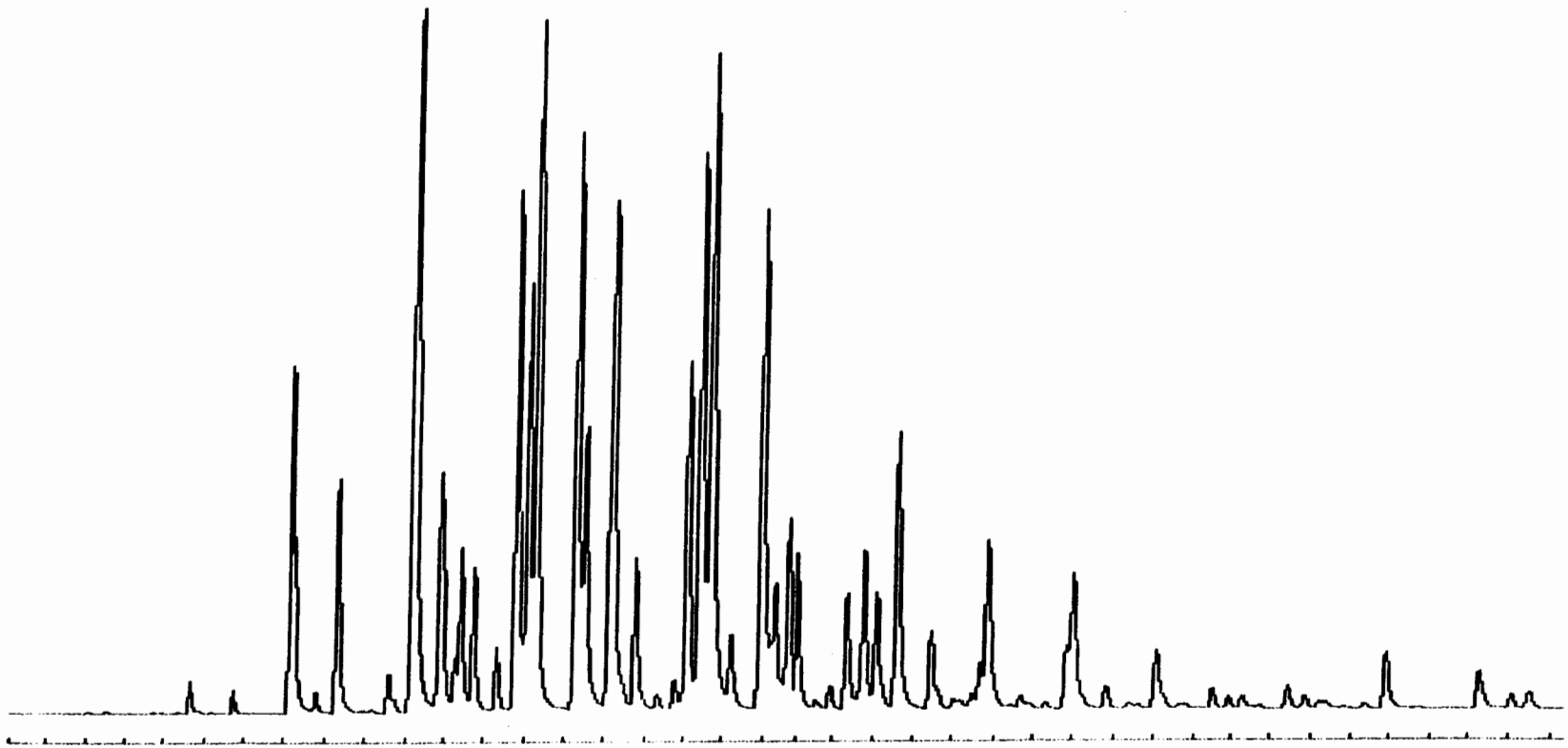
IME 10.00

AROCLOR 1242 STANDARD



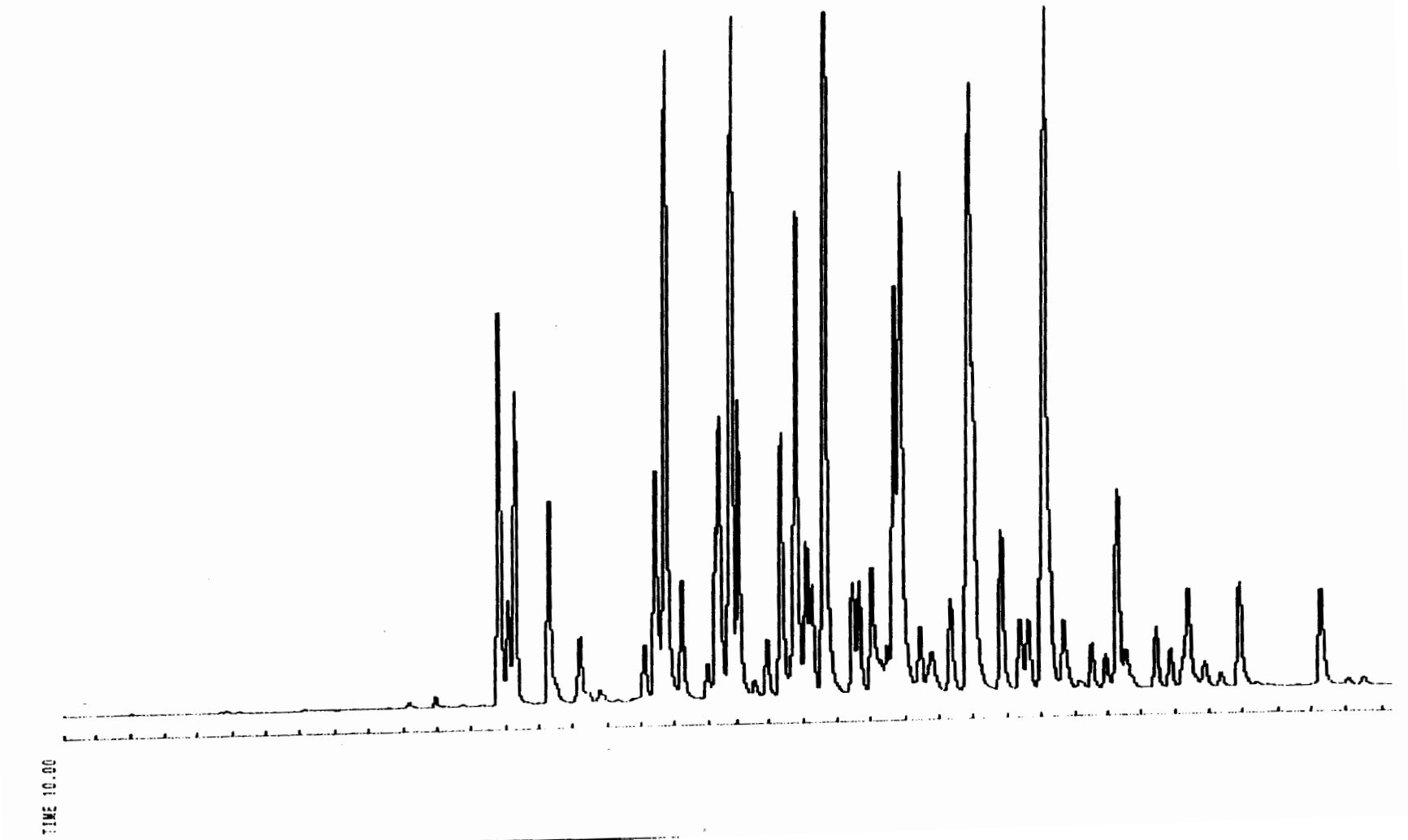
TIME 10.00

AROCLOR 1248 Standard

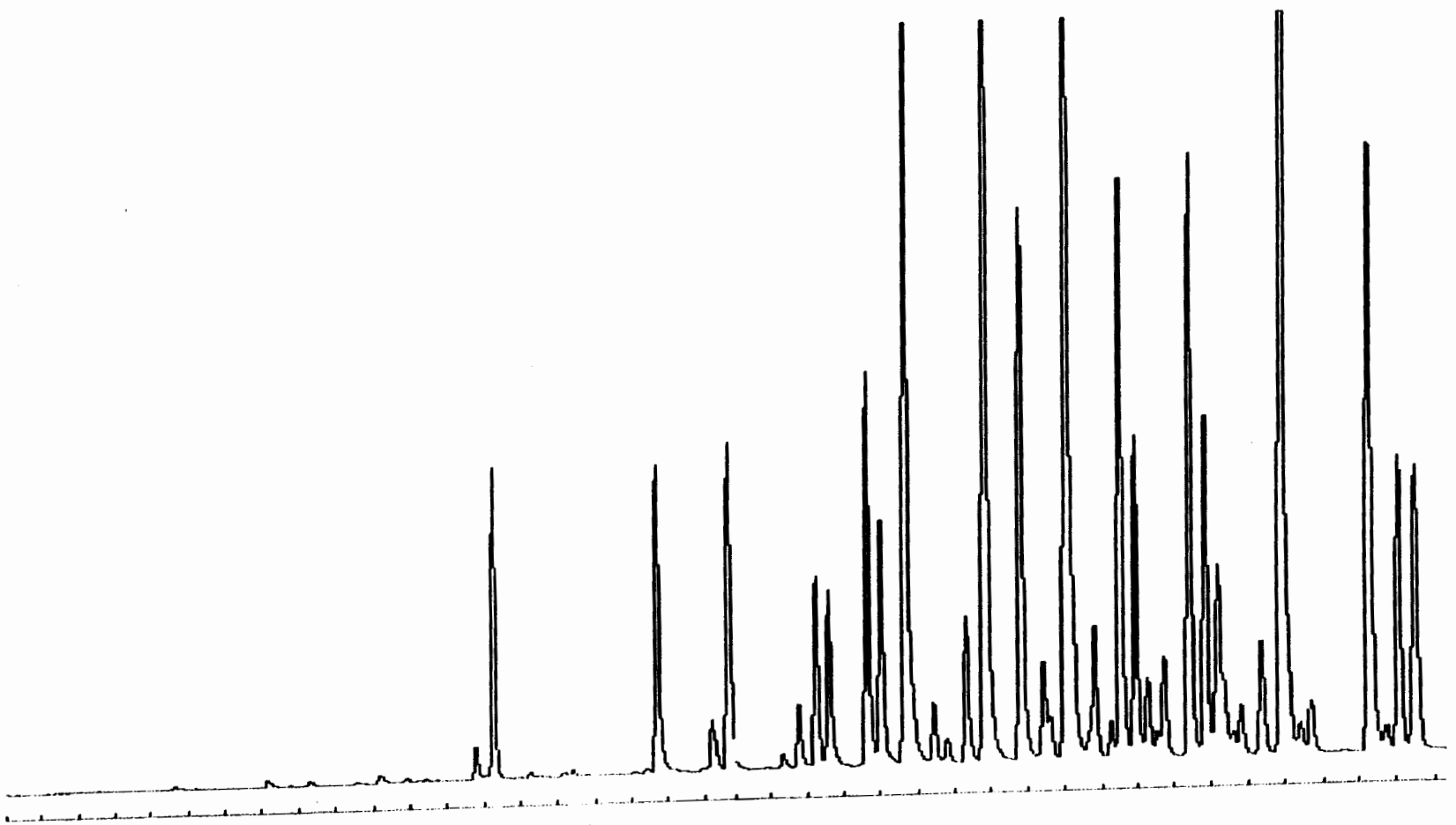


TIME 10.00

AROCLOR 1254 Standard



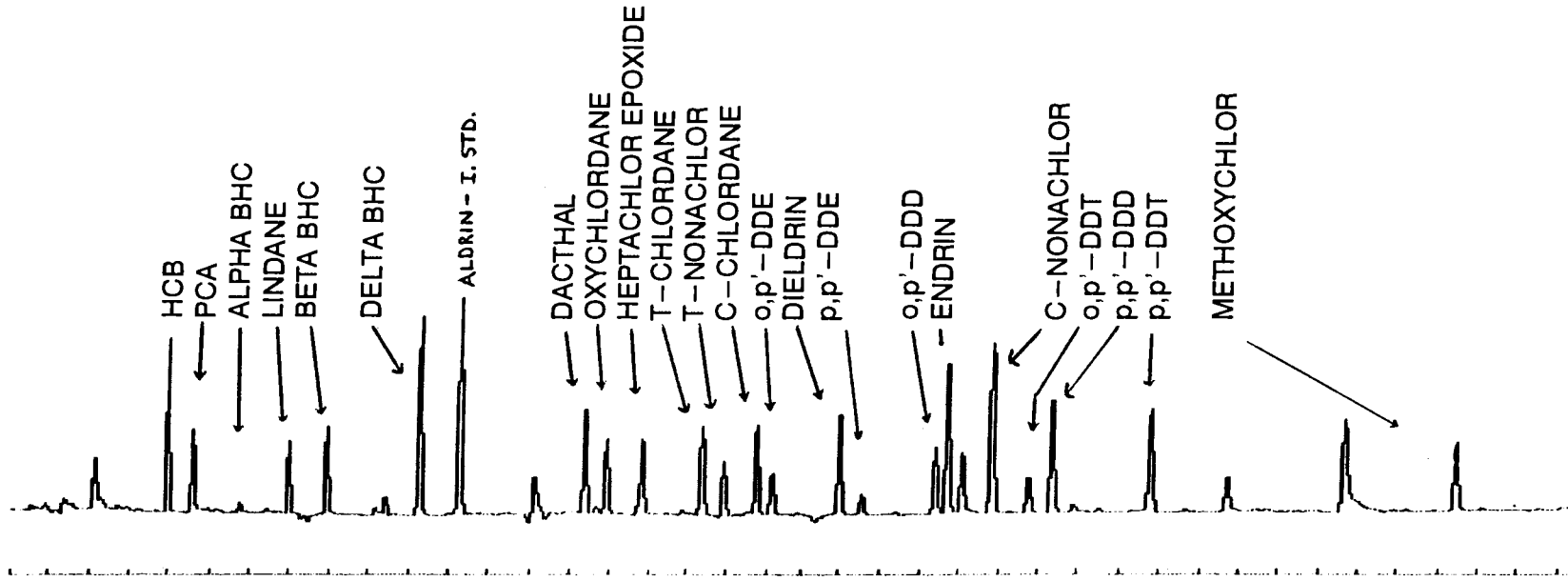
AROCLOR 1260 Standard



TIME 10.00

REAGENT SPIKE- OC PESTICIDES
SG-2 Fraction

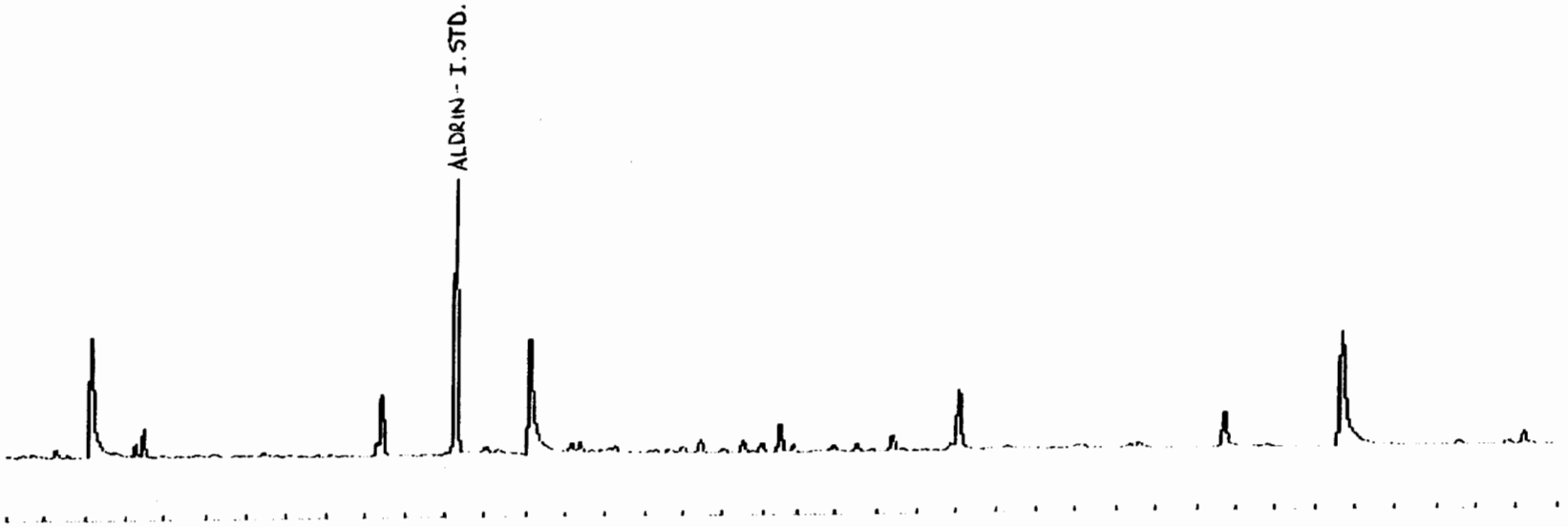
GC-ECD (OV-17)
Scale 100



TIME 10.00

REAGENT BLANK
SG-2 Fraction

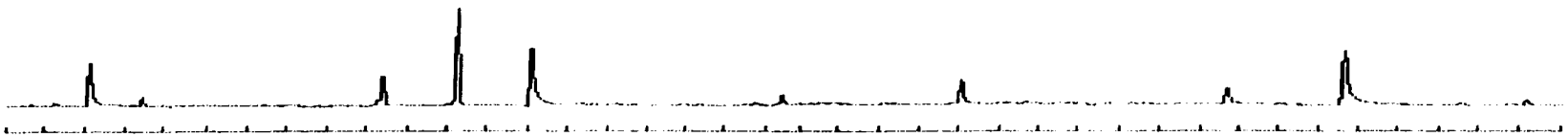
GC-ECD (OV-17)
Scale 300



TIME 10.00

PROCESS BLANK
SG-2 Fraction

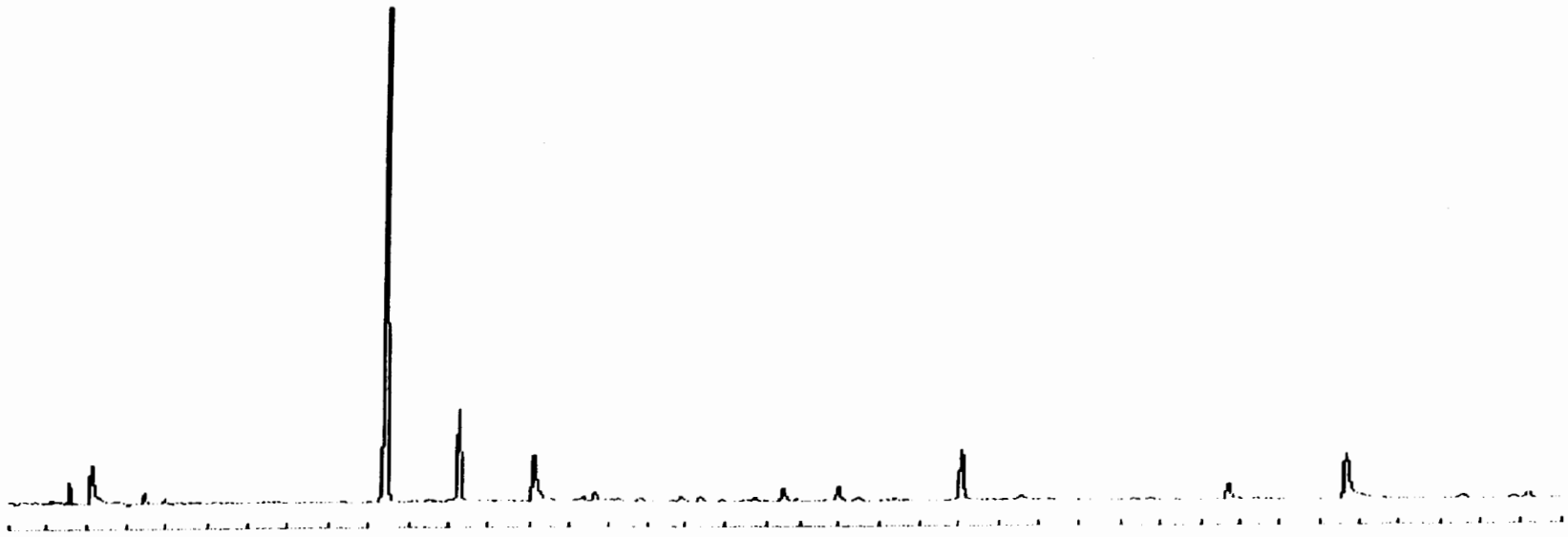
GC-ECD (OV-17)
Scale 300



TIME 10.00

SPMD LAB BLANK
SG-2 Fraction

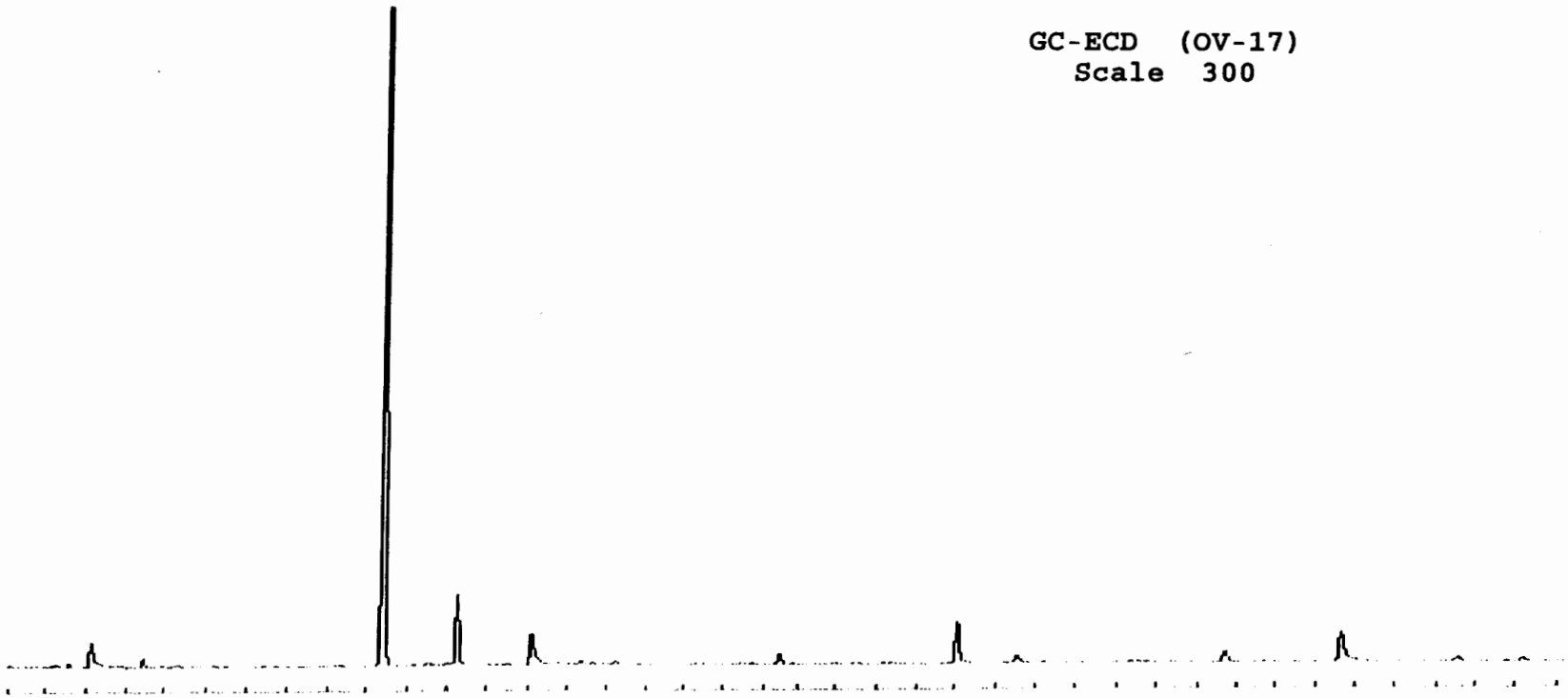
GC-ECD (OV-17)
Scale 300



TIME 10.00

FIELD BLANK- DAY 0
SG-2 Fraction

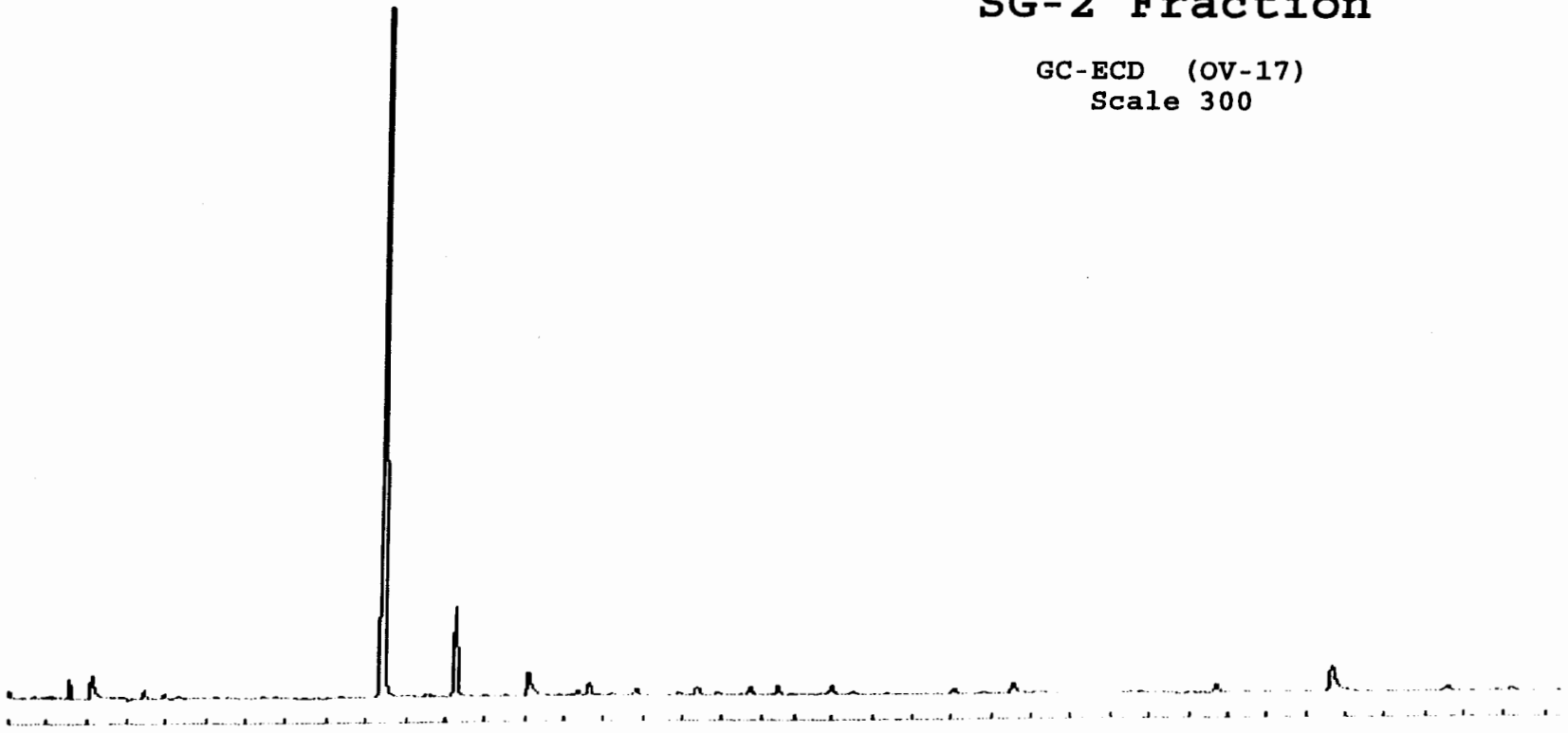
GC-ECD (OV-17)
Scale 300



TIME 10.00

FIELD BLANK- DAY 28
SG-2 Fraction

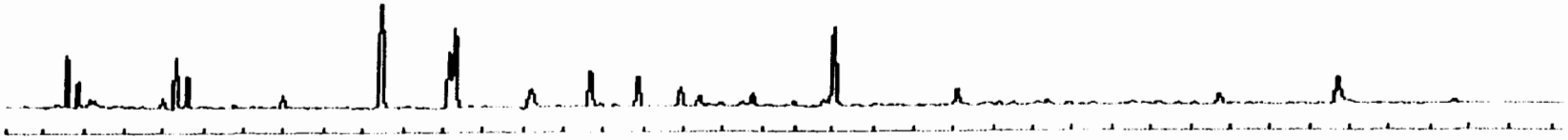
GC-ECD (OV-17)
Scale 300



TIME 10.00

SIOUX CITY SPMDs
SG-2 Fraction

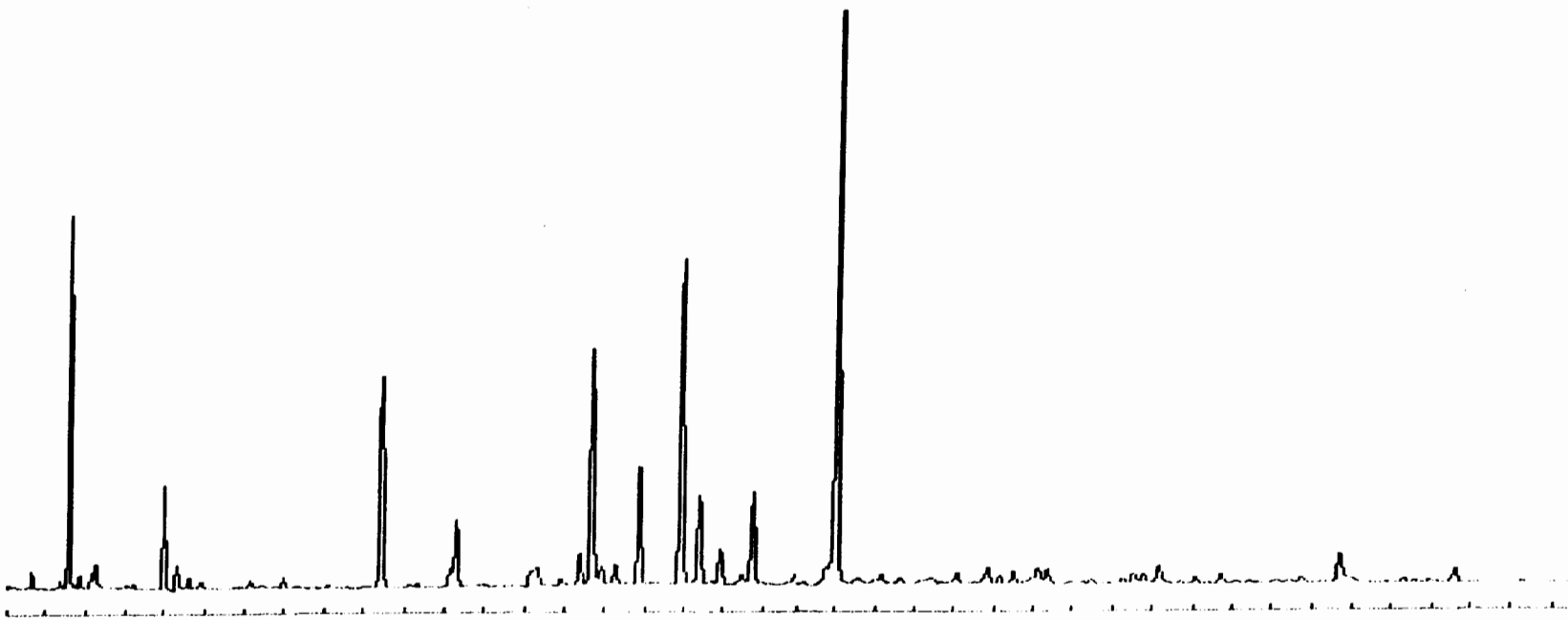
GC-ECD (OV-17)
Scale 300



TIME 10.00

NEBRASKA CITY SPMDs
SG-2 Fraction

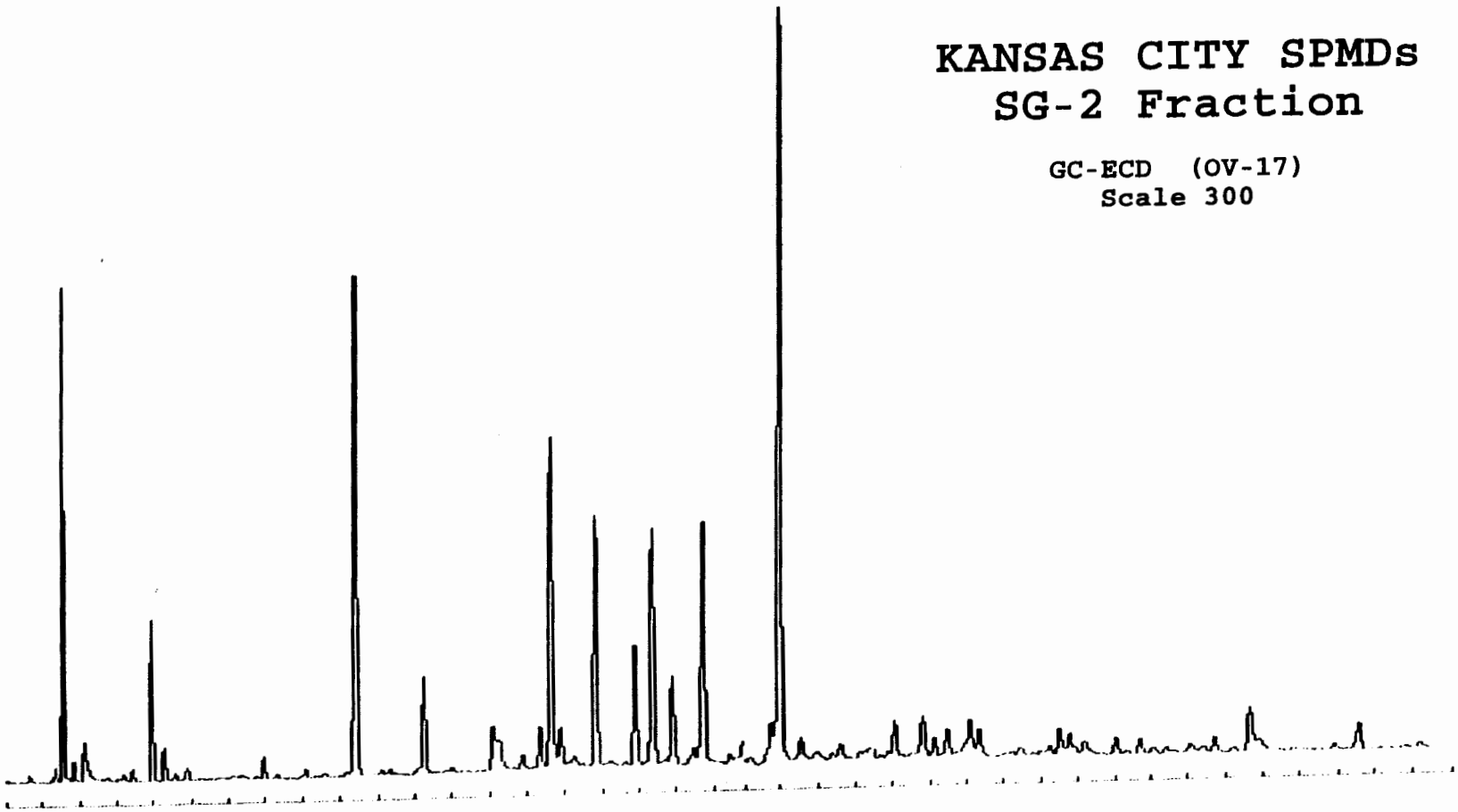
GC-ECD (OV-17)
Scale 300



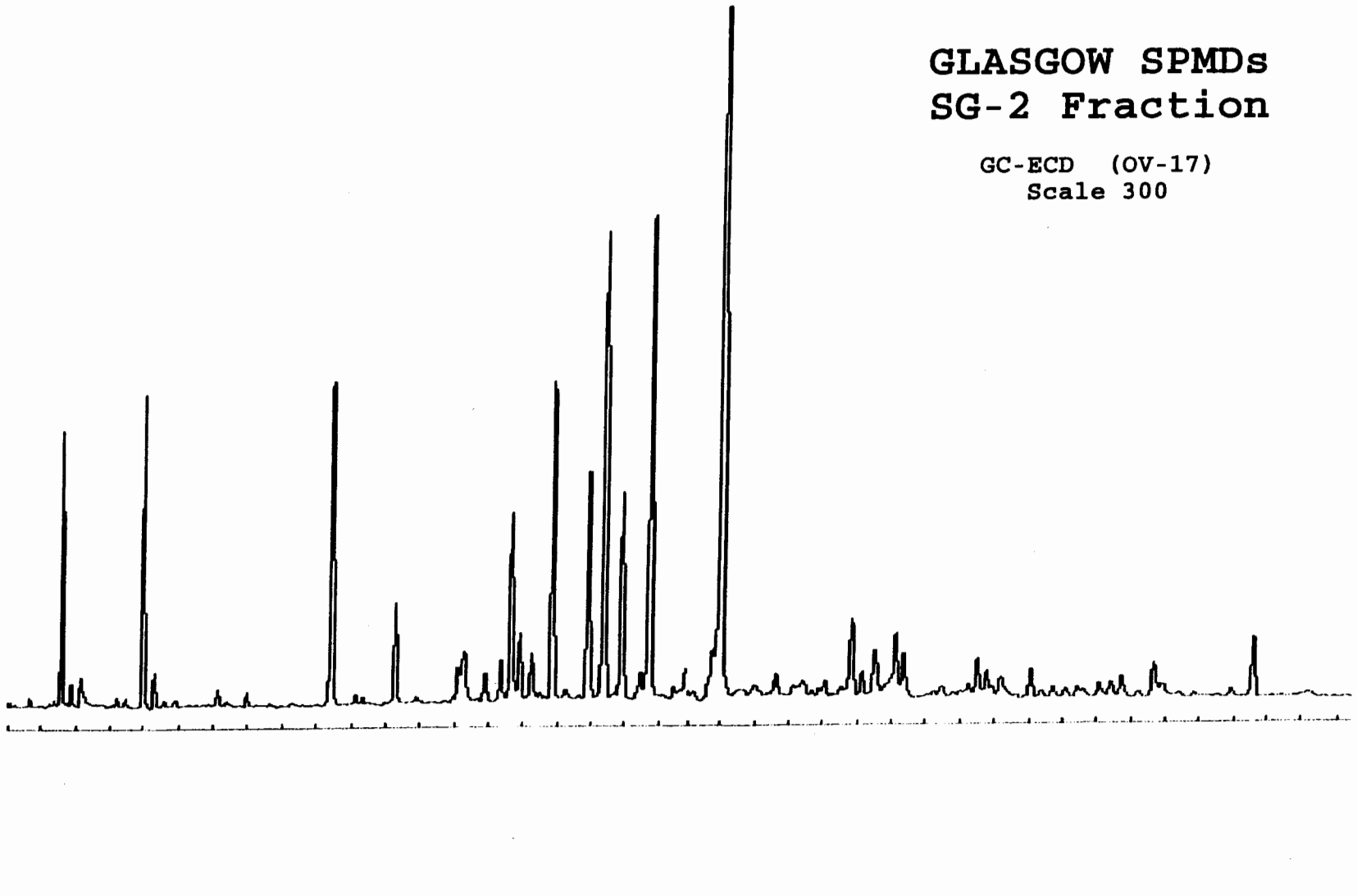
TIME 10.00

KANSAS CITY SPMDs
SG-2 Fraction

GC-ECD (OV-17)
Scale 300

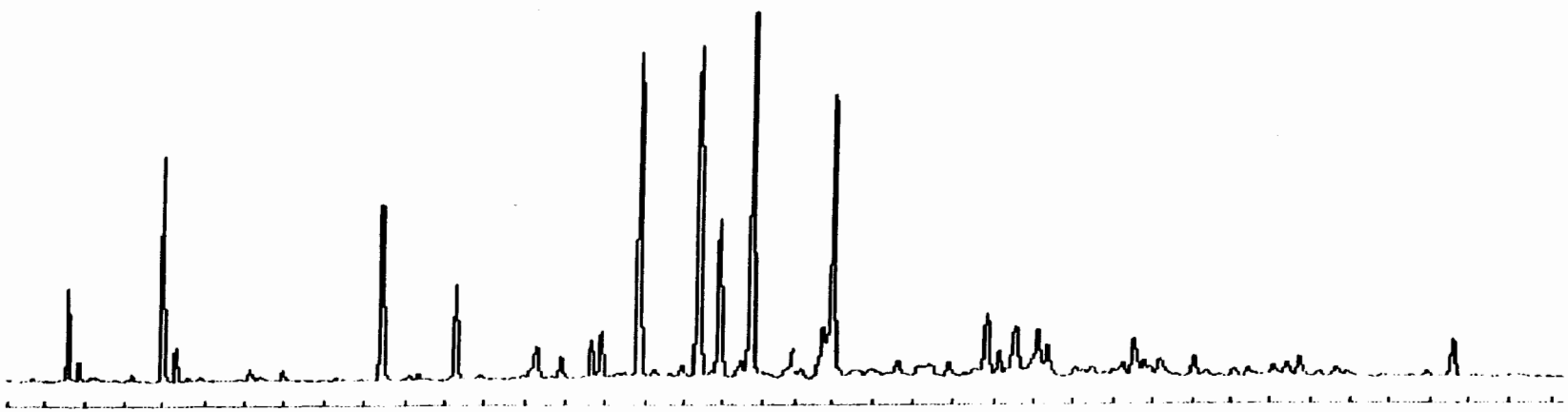


TIME 10.00


GLASGOW SPMDs
SG-2 Fraction
GC-ECD (OV-17)
Scale 300
TIME 10.00

HERMANN SPMDs
SG-2 Fraction

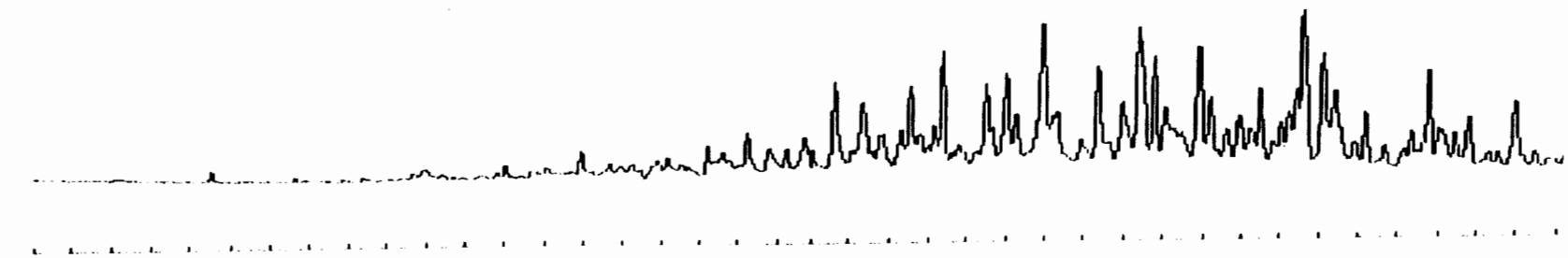
GC-ECD (OV-17)
Scale 300



TIME 10.00

TOXAPHENE STANDARD
SG-2 Fraction

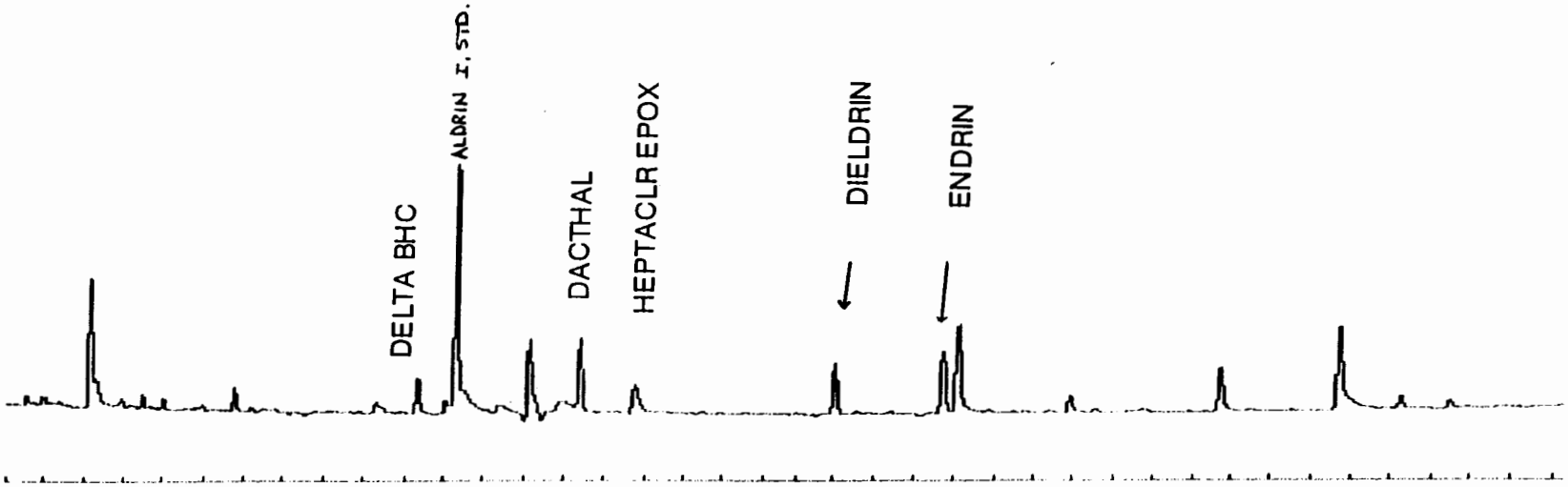
GC-ECD (OV-17)
Scale 25



TIME 10.00

REAGENT SPIKE
FL-2 Fraction

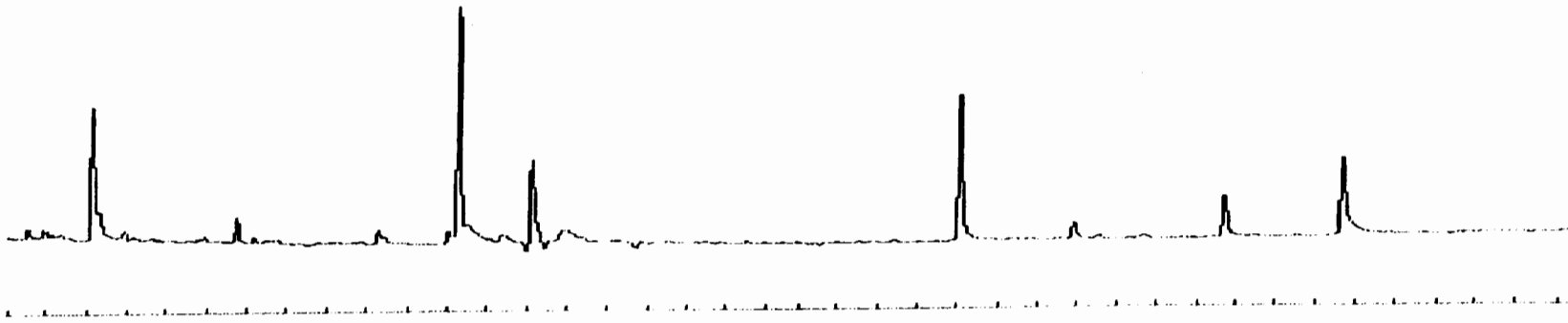
GC-ECD (DB5)
Scale 100



TIME 10.00

REAGENT BLANK
FL-2 Fraction

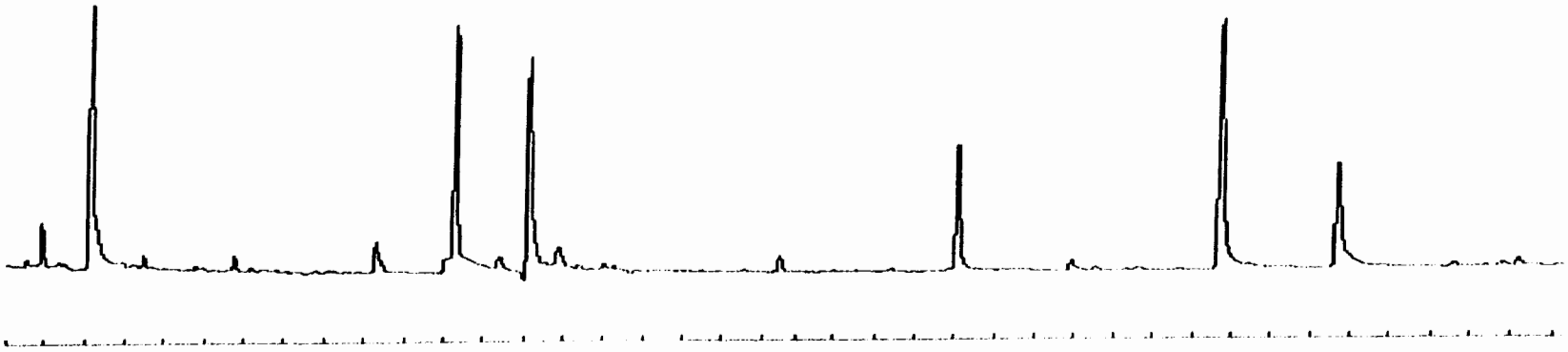
GC-ECD (DB5)
Scale 100



TIME 10.00

PROCESS BLANK
FL-2 Fraction

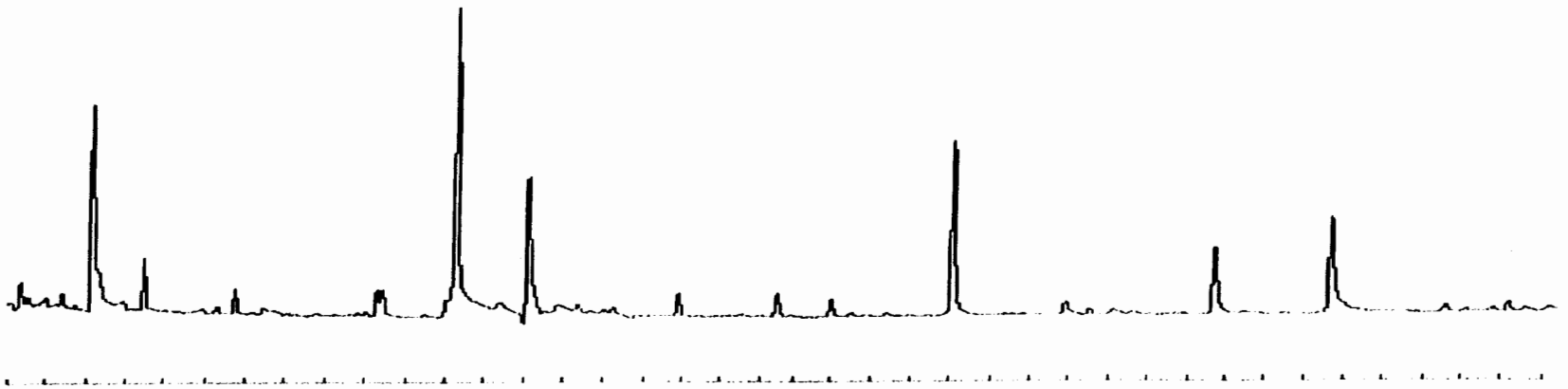
GC-ECD (DB5)
Scale 100



TIME 10.00

SPMD LAB BLANK
FL-2 Fraction

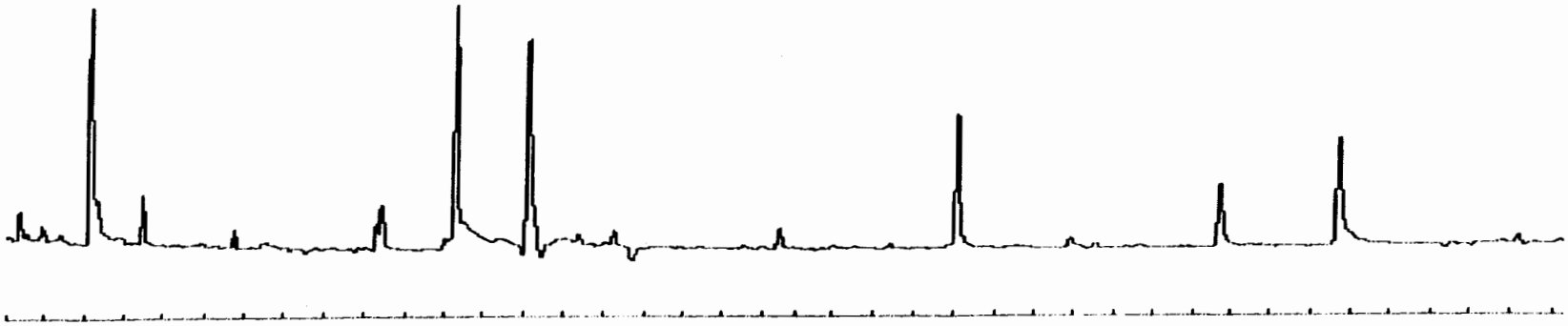
GC-ECD (DB5)
Scale 100



TIME 10.00

FIELD BLANK- DAY 0
FL-2 Fraction

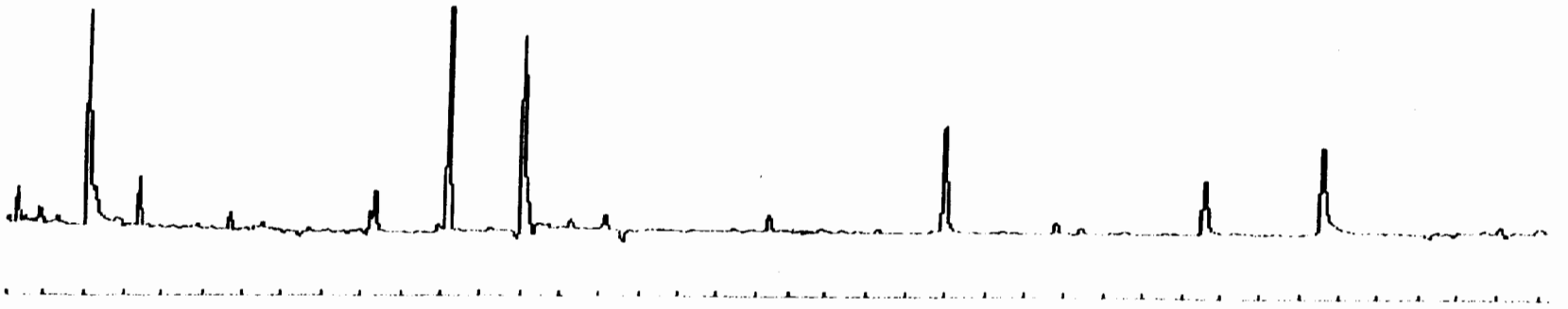
GC-ECD (DB5)
Scale 100



TIME 10.00

FIELD BLANK- DAY 28
FL-2 Fraction

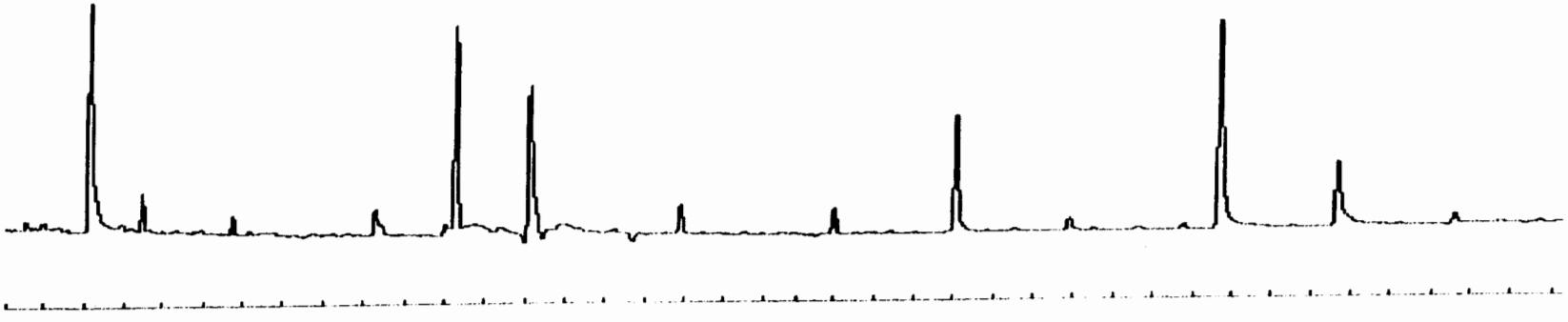
GC-ECD (DB5)
Scale 100



TIME 10.00

SIOUX CITY SPMDs
FL-2 Fraction

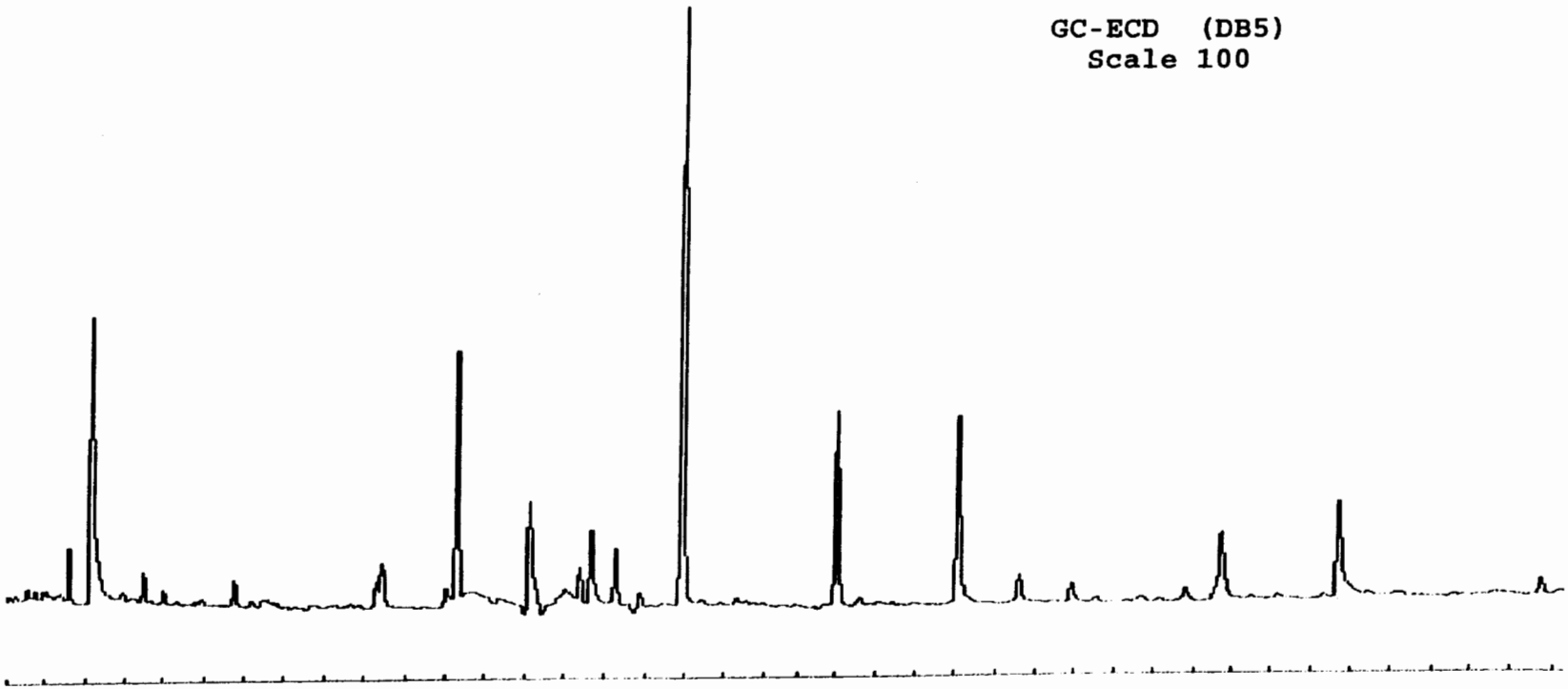
GC-ECD (DB5)
Scale 100



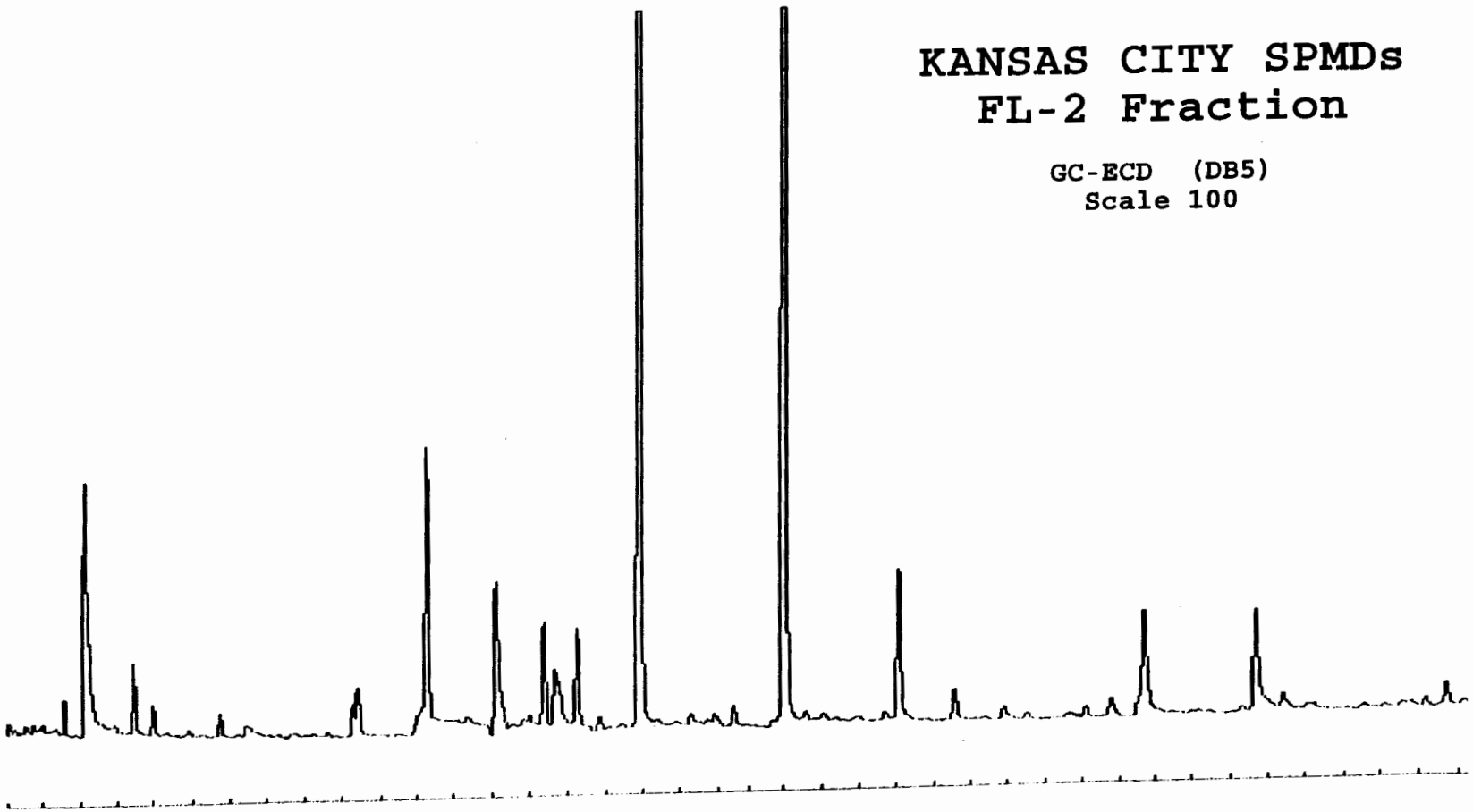
TIME 10.00

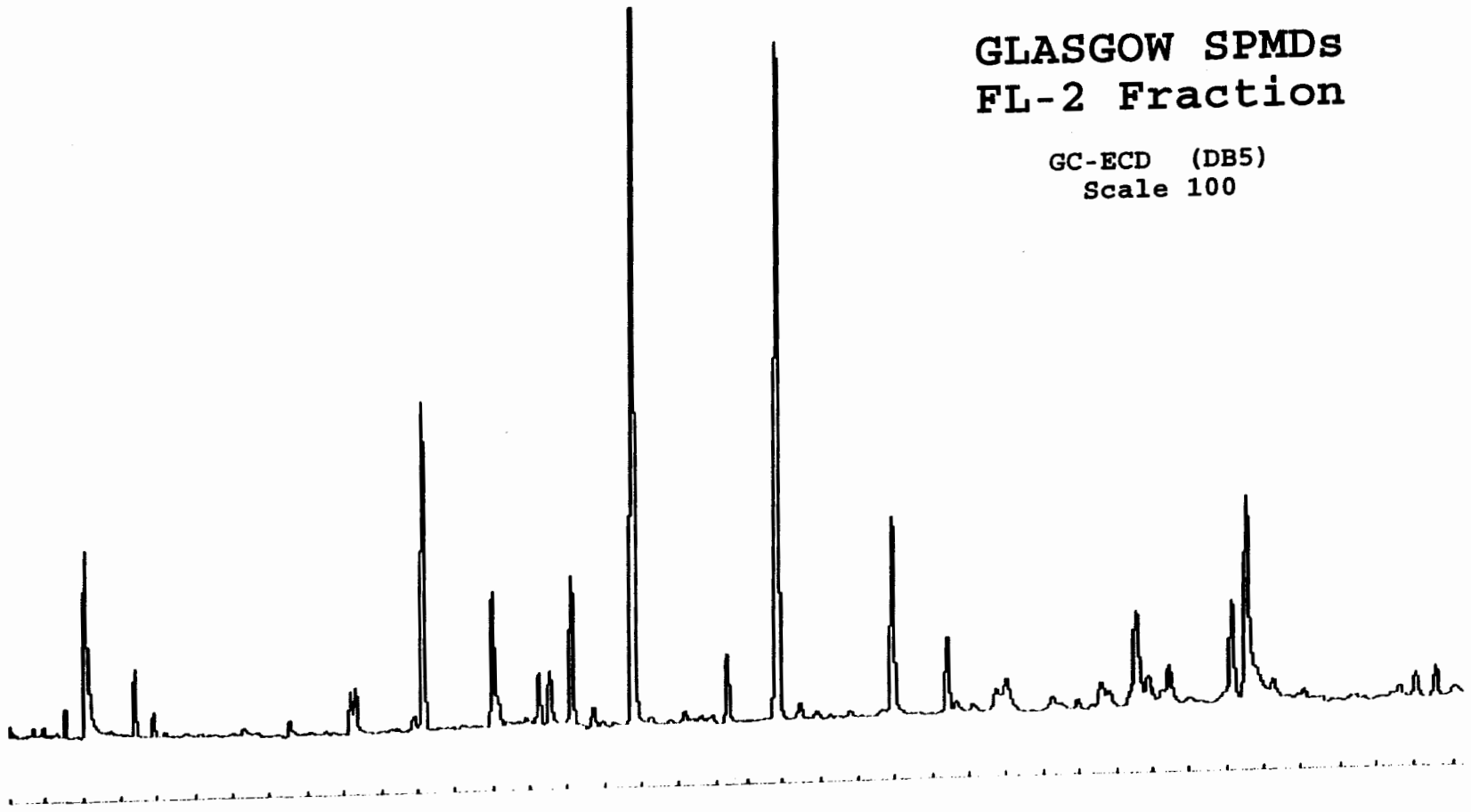
NEBRASKA CITY SPMDs
FL-2 Fraction

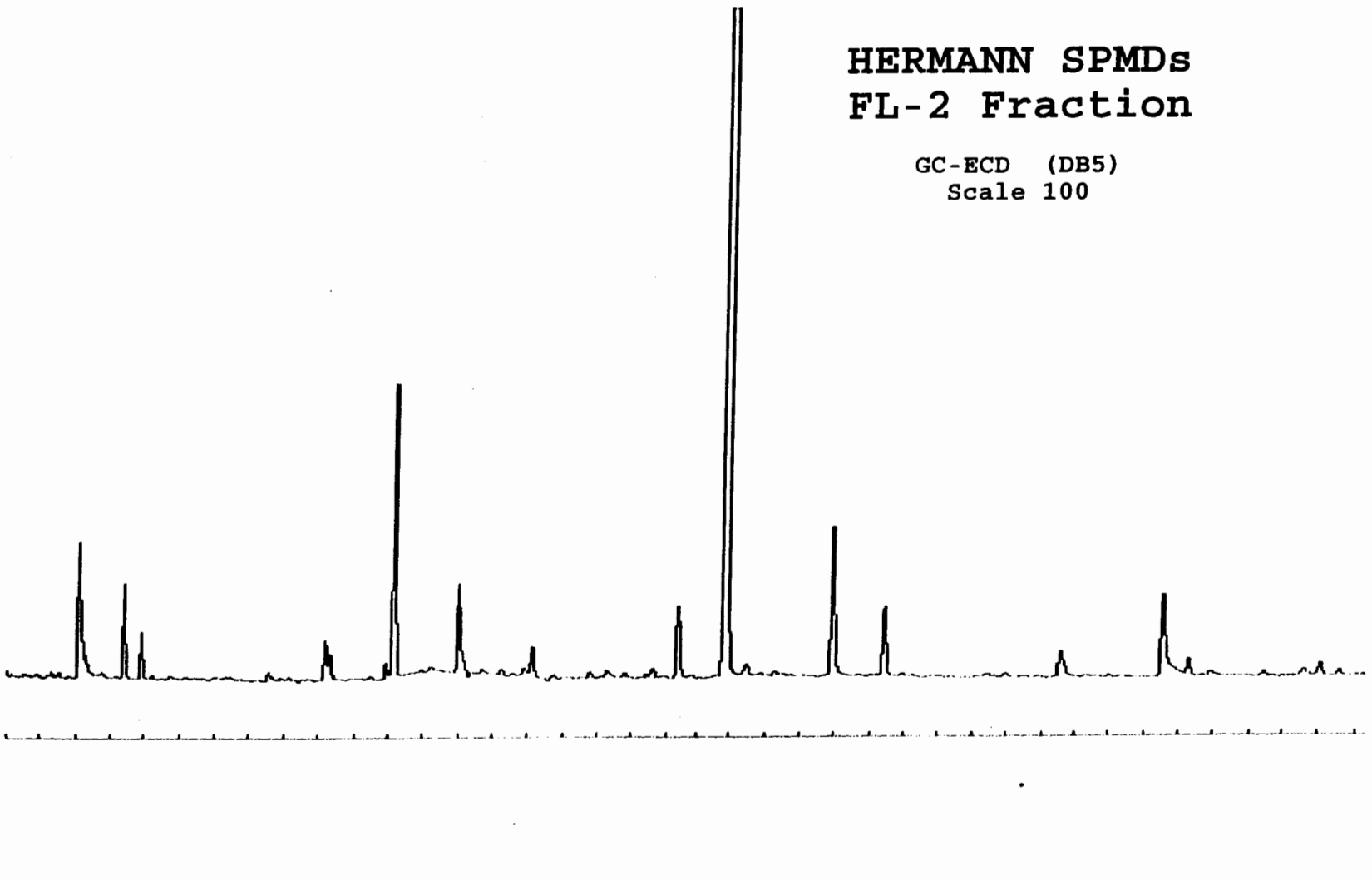
GC-ECD (DB5)
Scale 100



TIME 10.00


KANSAS CITY SPMDs
FL-2 Fraction
GC-ECD (DB5)
Scale 100
TIME 10.00

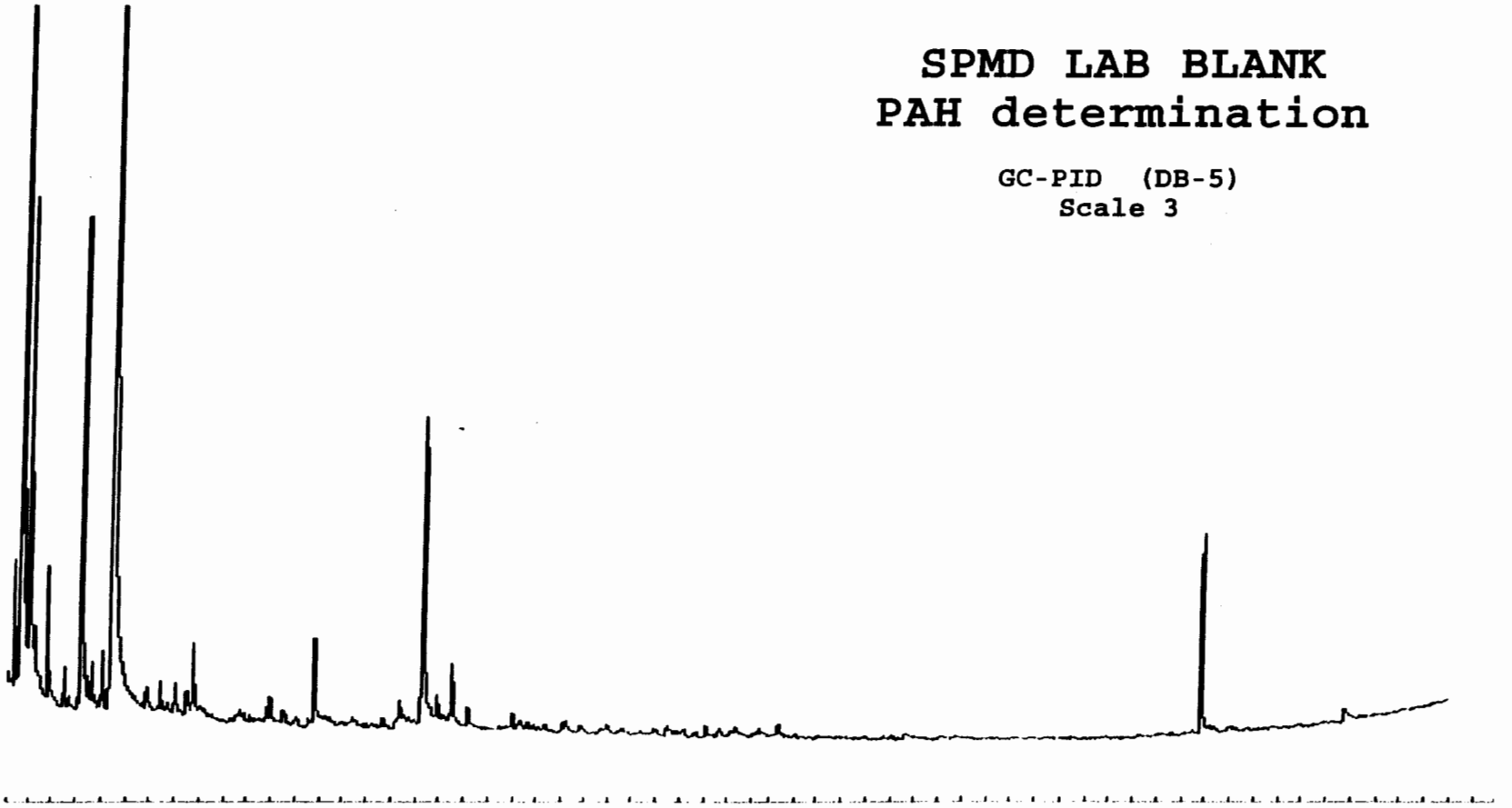

GLASGOW SPMDs
FL-2 Fraction
GC-ECD (DB5)
Scale 100
TIME 10.00


HERMANN SPMDs
FL-2 Fraction
GC-ECD (DB5)
Scale 100
TIME 10.00

REAGENT SPIKE
PAH determination
GC-PID (DB-5)
Scale 6
naphthalene
I.STD. AZULENE
acenaphthalene
acenaphthene
fluorene
phenanthrene
anthracene
fluoranthene
pyrene
benzo(a)anthracene
chrysene
bz(b)fluoranthene
bz(k)fluoranthene
benzo(a)pyrene
indeno(123cd)pyrene
dibz(ah)anthracene
benzo(ghi)perylene
TIME 4.00

SPMD LAB BLANK
PAH determination

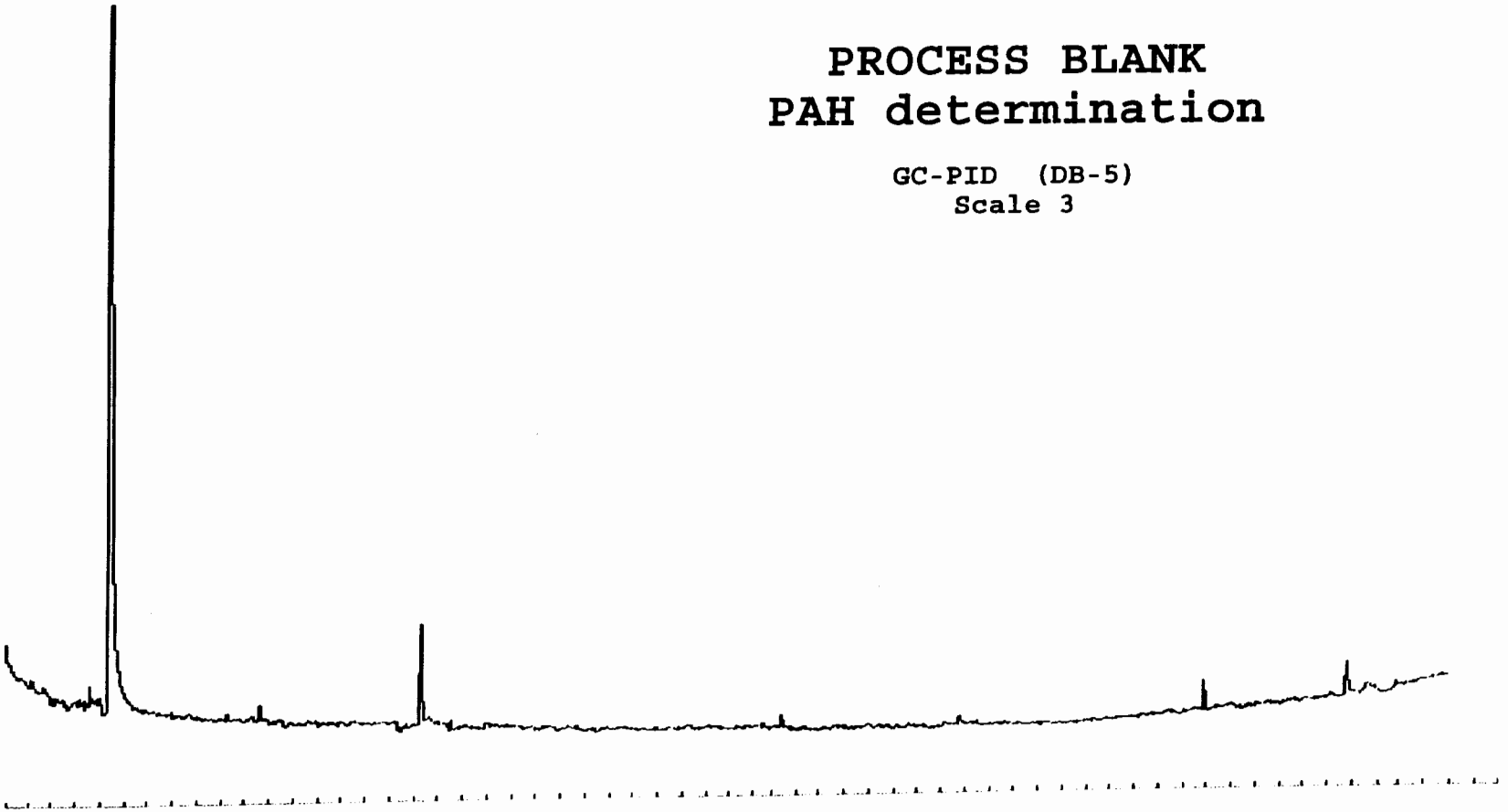
GC-PID (DB-5)
Scale 3



TIME 4.00

PROCESS BLANK
PAH determination

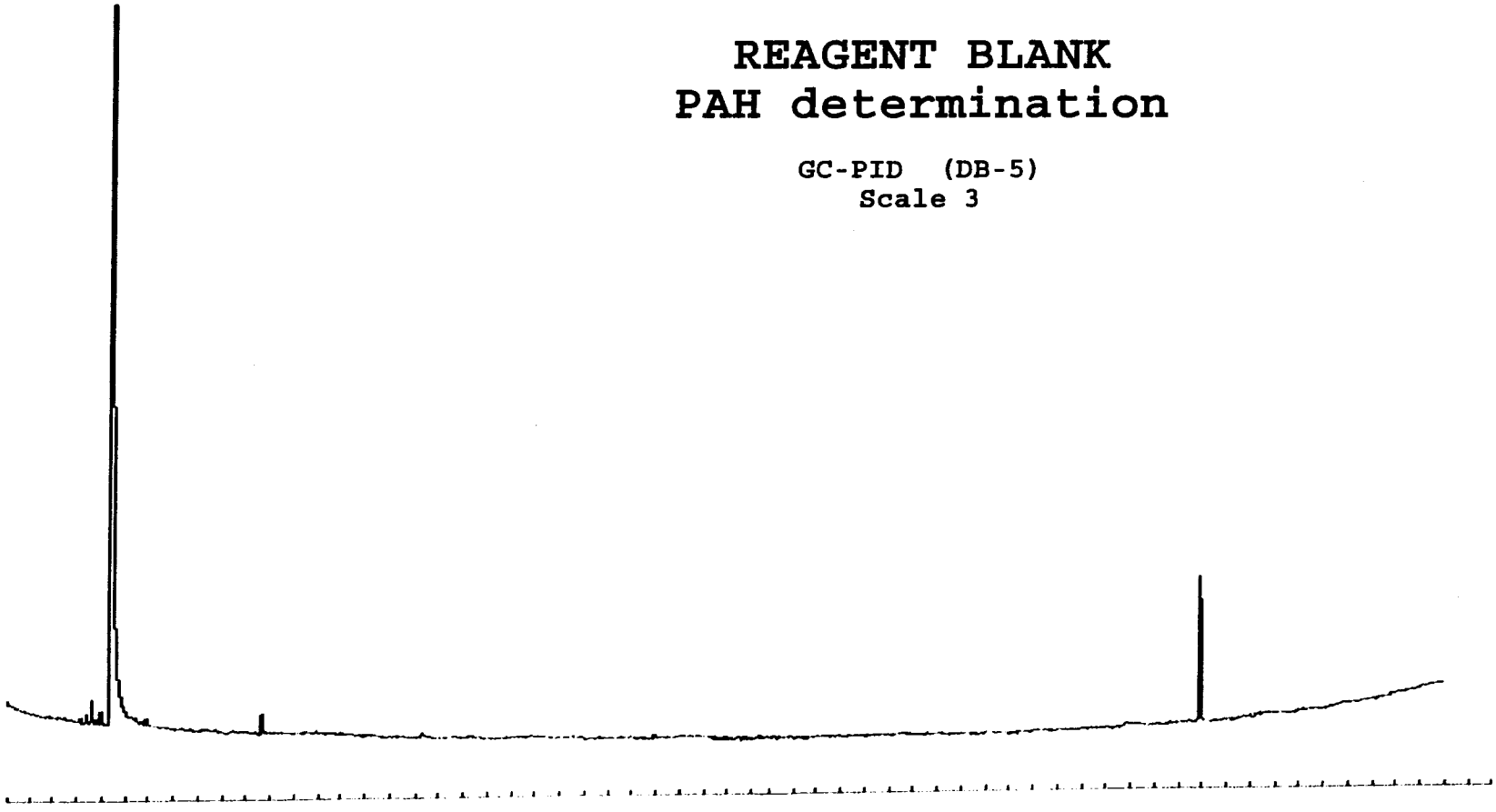
GC-PID (DB-5)
Scale 3



TIME 4.00

REAGENT BLANK
PAH determination

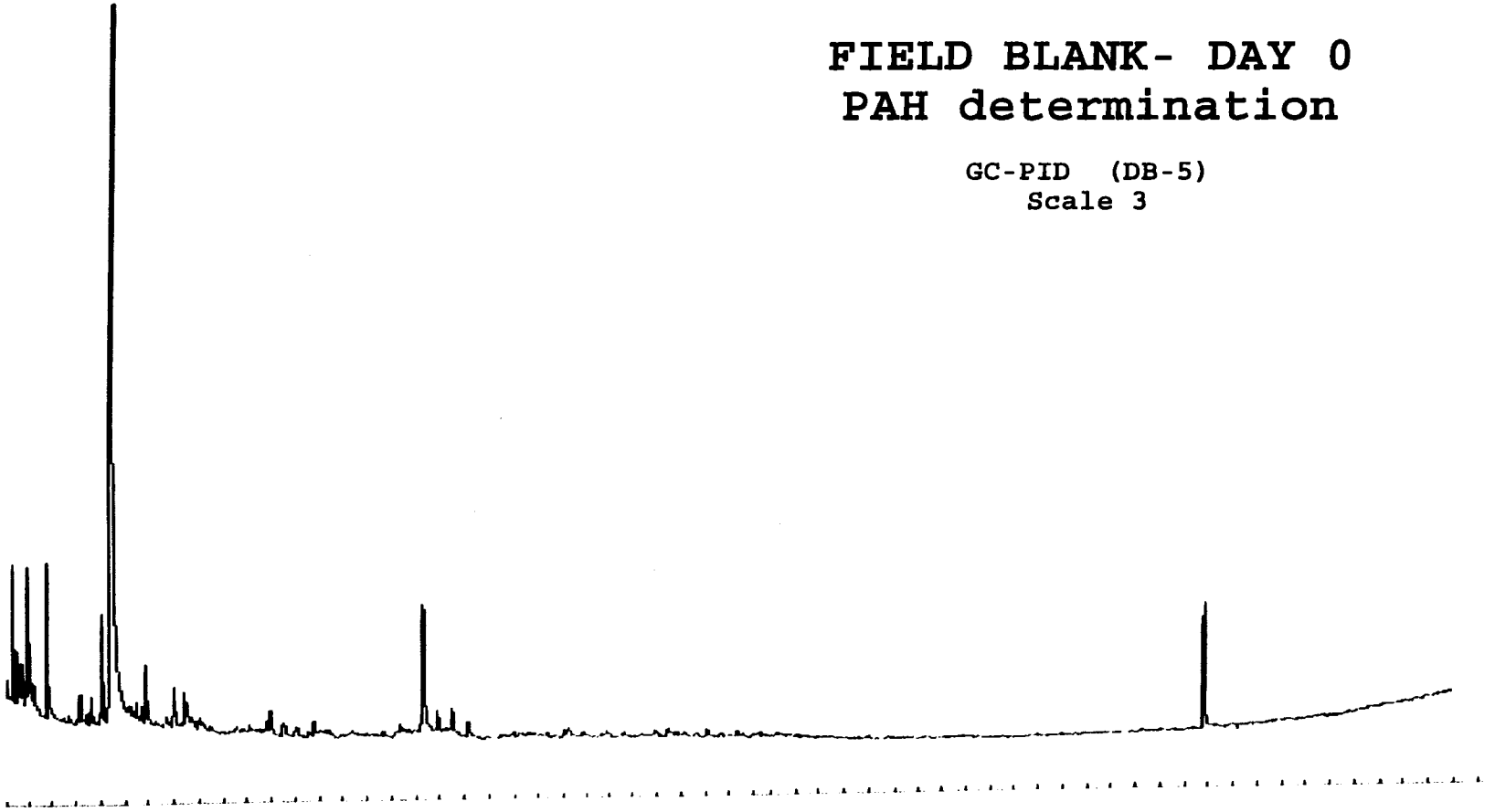
GC-PID (DB-5)
Scale 3



TIME 4.00

FIELD BLANK- DAY 0
PAH determination

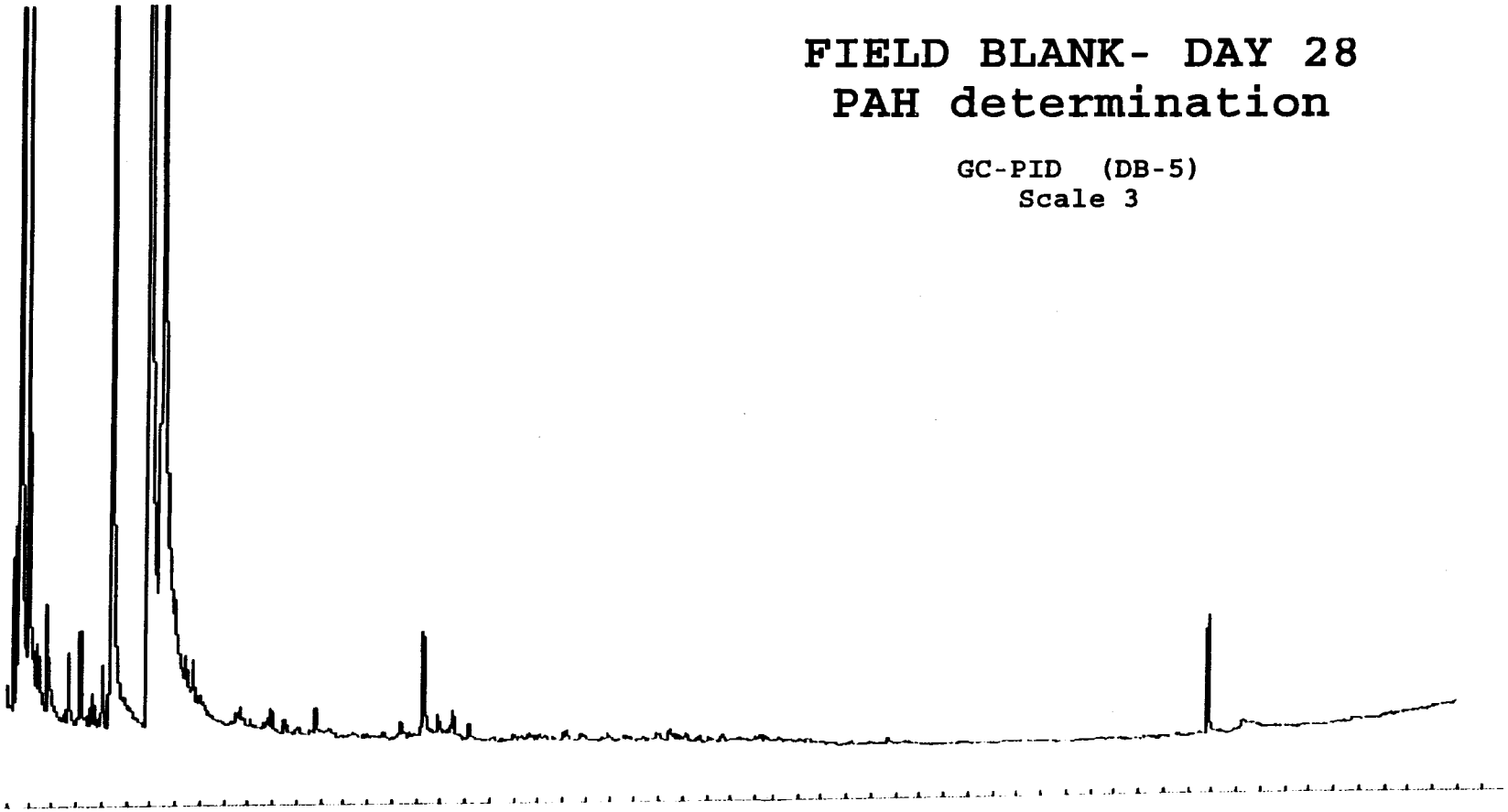
GC-PID (DB-5)
Scale 3



TIME 4.00

FIELD BLANK- DAY 28
PAH determination

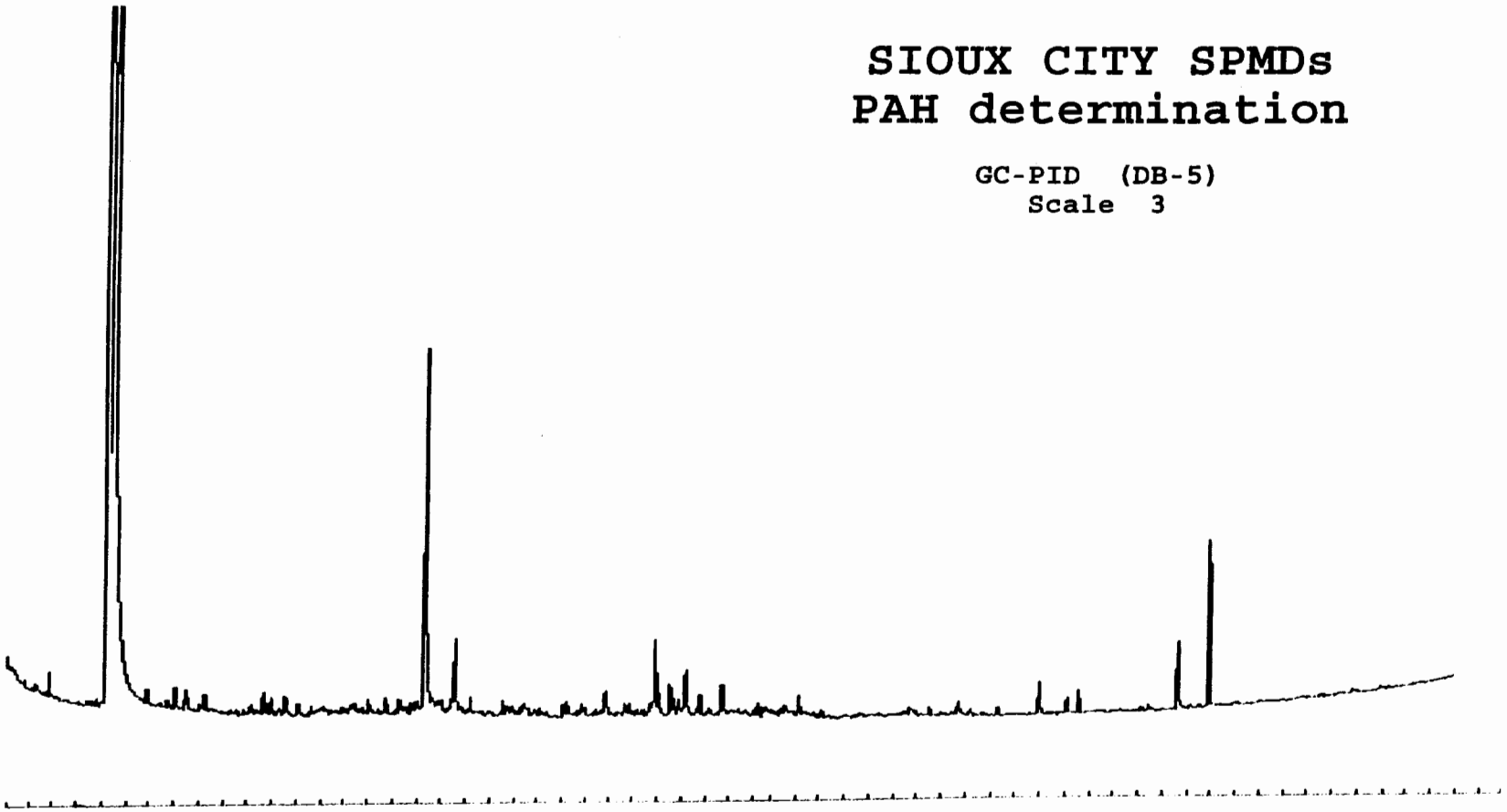
GC-PID (DB-5)
Scale 3



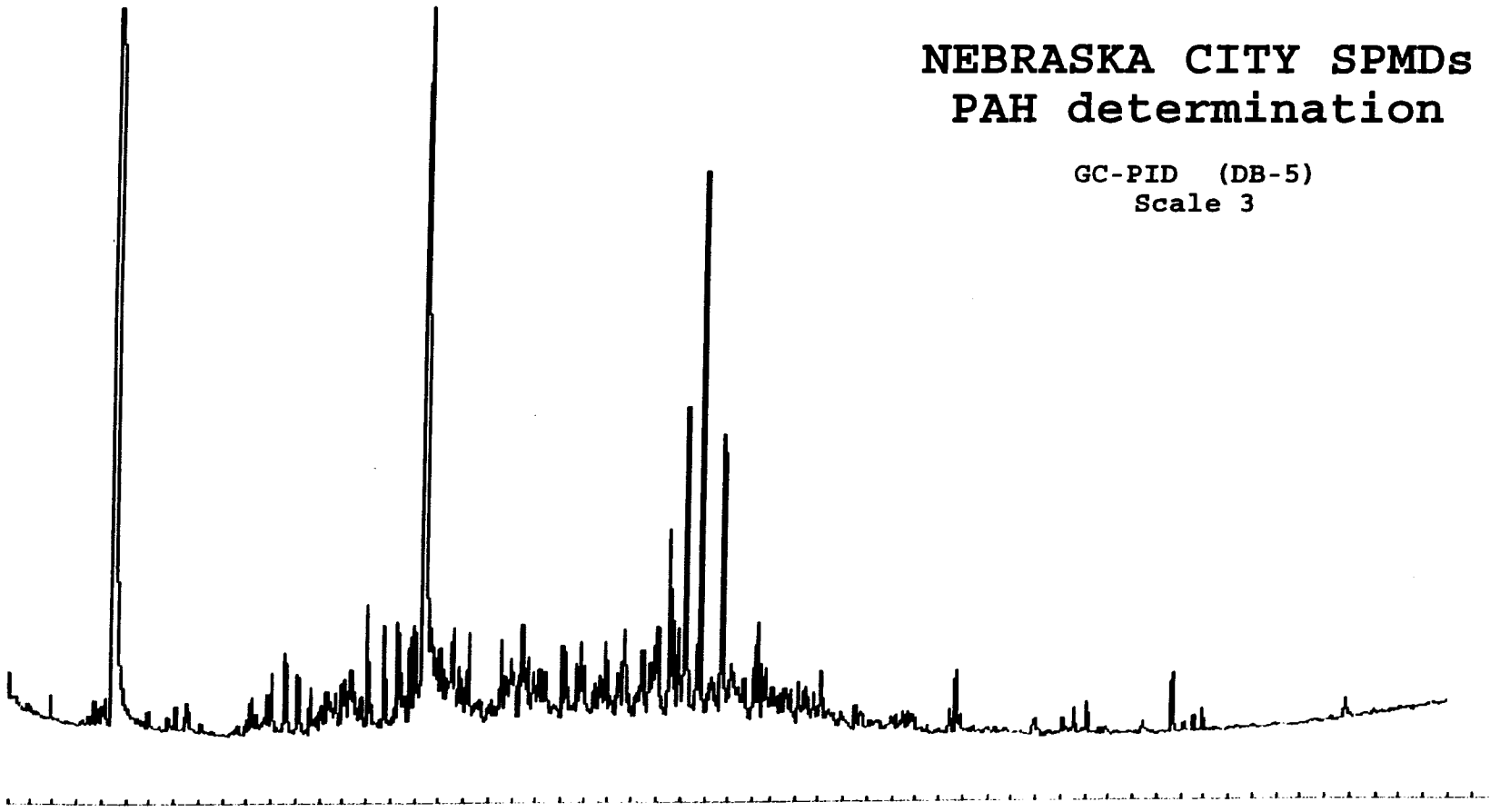
TIME 4.00

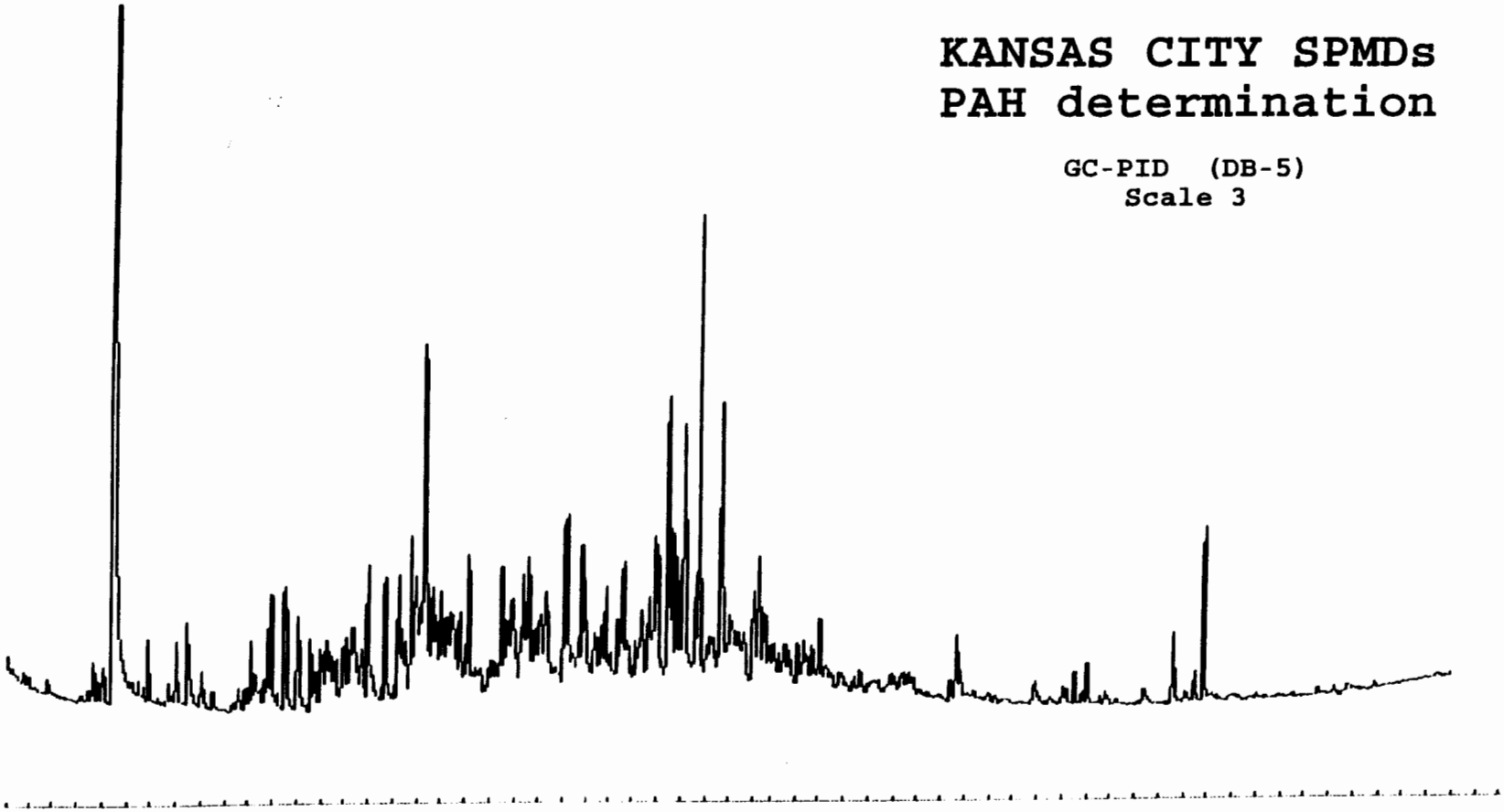
SIOUX CITY SPMDs
PAH determination

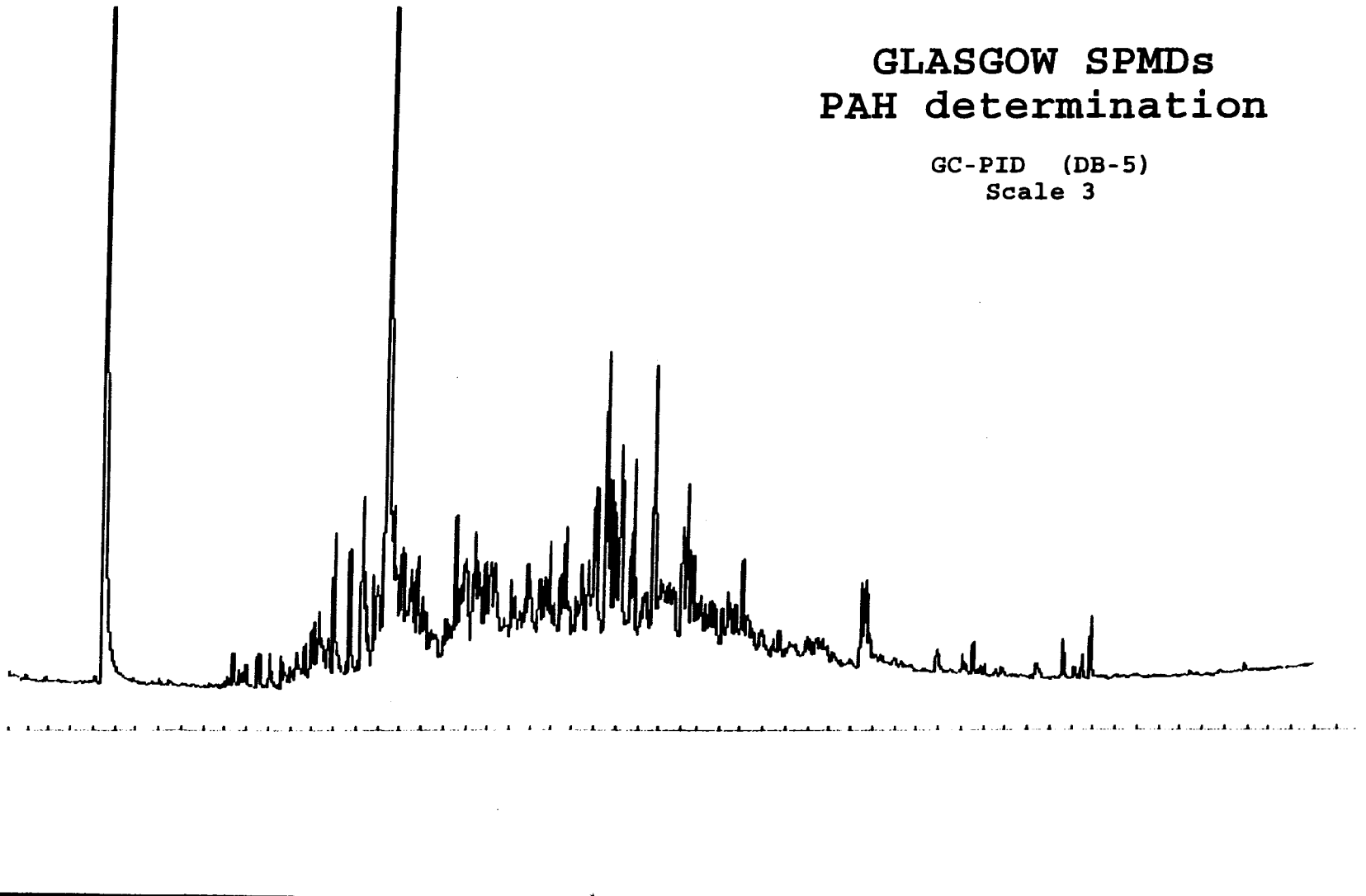
GC-PID (DB-5)
Scale 3

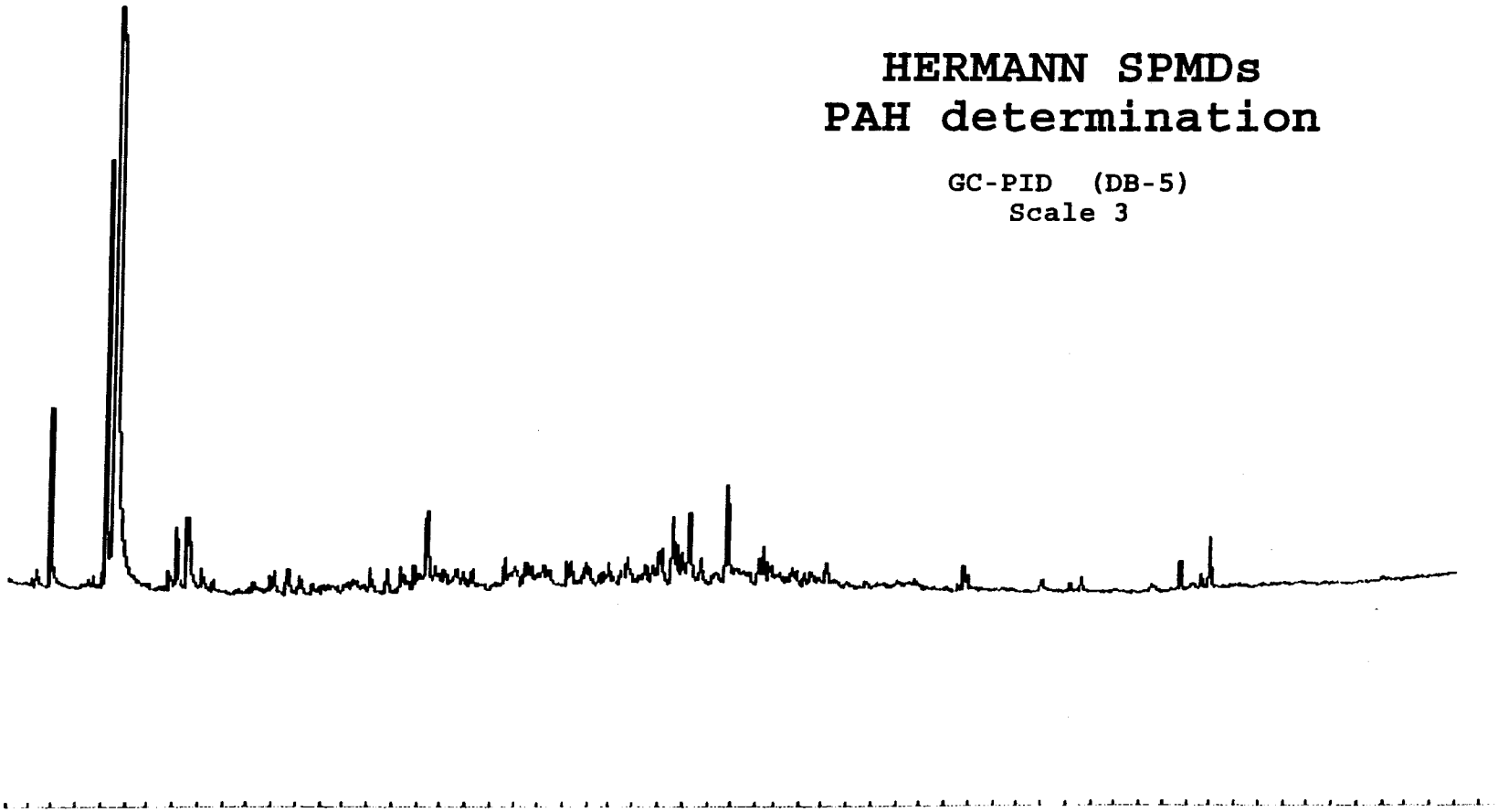


TIME 4.00


NEBRASKA CITY SPMDs
PAH determination
GC-PID (DB-5)
Scale 3
IME 4.00


KANSAS CITY SPMDs
PAH determination
GC-PID (DB-5)
Scale 3
TIME 4.00


GLASGOW SPMDs
PAH determination
GC-PID (DB-5)
Scale 3
TIME 4.00


HERMANN SPMDs
PAH determination
GC-PID (DB-5)
Scale 3
TIME 4.00

Method file name: G:H14EY9
Default Sample Name: Missouri River SPMD PRoject- ENV Chem
Operator: CEOrazio
Date-time: 07-20-1993 15:38:44 version: 501

ACQUISITION PARAMETERS

SINGLE OR DUAL CHANNEL (1 OR 2)	1.00
RUN TIME (minutes)	68.00
END TIME FOR PLOTS (default=RUN TIME)	68.00
SOLVENT DELAY TIME (minutes)	0.00
PEAK DETECTION THRESHOLD (microv/sec)	1.00
Area Threshold	100.00
MINIMUM PEAK WIDTH (seconds)	10.00
TIME FOR ONE SAMPLE (seconds)	0.80
NUMBER OF REAL TIME CRT PAGES TO PLOT (0 TO 99)	1.00
REAL TIME PLOT FULL SCALE FOR CH.0 (millivolts)	100.00
REAL TIME FULL SCALE FOR CH.1 (millivolts)	200.00
HARD COPY REAL TIME PLOT	YES
AUTO ZERO REAL TIME PLOT	NO
Pre Version 4 method	YES
RECORD AREA TABLES ON DISK	NO
RECORD RAW DATA	YES
NUMBER OF CRT PAGES FOR REPLOT (1 TO 99)	0.00
VERTICAL SCALE FACTOR FOR REPLOT (units of largest peak)	3.00
OFFSET FOR THE REPLOT (millivolts)	0.00
PUT NAMES ON REPLOT?	YES
PRINT AREA PERCENT REPORT	NO
PRINT EXTERNAL STANDARD REPORT	NO
PRINT INTERNAL STANDARD REPORT	YES
FINAL REPORT AREA REJECT (microvolt-sec)	800.00
LINK TO USER PROGRAM	YES
FORCE DROP LINE INTEGRATION	NO
FORCE COMMON BASE LINE	NO
FULL SCALE RANGE FOR A.D.C. (3=1VOLT, 1=2VOLT, 0=10VOLT)	3.00
AREA REJECT FOR REFERENCE PEAKS?	30000.00
% RET TIME WINDOW FOR REFERENCE PEAKS	0.20
RET TIME WINDOW IN SECONDS FOR REF. PEAKS	2.00
AREA OR PEAK HEIGHT QUANTITATION (0 OR 1)	0.00
PRINT GROUP REPORT	NO
NUMBER OF CALIBRATION LEVELS (1 TO 6)	5.00
LIST COMPONENTS NOT FOUND IN SAMPLE?	YES
INCLUDE UNKNOWN PEAKS IN REPORTS?	NO
UPDATE RESPONSE FACTORS WITH REPLACEMENT (0) OR AVERAGE (1)	1.00
DEFAULT DILUTION FACTOR	1.00
DEFAULT SAMPLE WEIGHT	1.00
DEFAULT AMOUNT INJECTED	1.00
DEFAULT AMOUNT OF INTERNAL STANDARD	20.00
PRINT GPC MW DISTRIBUTION	NO
PRINT SIMULATED DISTILLATION REPORT	NO

LINK TO PROGRAM QUREPORT!
SAVE RAW DATA IN: G:H14EY.PTS
Response factor for unknowns= 1.0000E-04
Component Units = ng/smpl

1 HCB Ret. Time = 13.51 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	50532	2.50000	0.00004947
2	102117	5.00000	0.00004896
3	195582	10.00000	0.00005113
4	304001	20.00000	0.00006579
5	629832	40.00000	0.00006351

2 PCA Ret. Time = 14.03 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	54256	2.50000	0.00004608
2	111274	5.00000	0.00004493
3	217657	10.00000	0.00004594
4	327812	20.00000	0.00006101
5	707047	40.00000	0.00005657

3 ALPHA BHC Ret. Time = 14.63 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	17016	2.50000	0.00014692
2	36709	5.00000	0.00013621
3	75938	10.00000	0.00013169
4	110794	20.00000	0.00018052
5	277054	40.00000	0.00014438

4 LINDANE Ret. Time = 17.01 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	17814	2.50000	0.00014034
2	37228	5.00000	0.00013431
3	73522	10.00000	0.00013601
4	110235	20.00000	0.00018143
5	263338	40.00000	0.00015190

5 BETA BHC Ret. Time = 18.00 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	23458	5.00000	0.00021314
2	48124	10.00000	0.00020780
3	92998	20.00000	0.00021506
4	129559	40.00000	0.00030874
5	280395	80.00000	0.00028531

6 HEPTACHLOR Ret. Time = 19.23 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	24207	2.50000	0.00010328
2	49265	5.00000	0.00010149
3	92224	10.00000	0.00010843
4	163746	20.00000	0.00012214
5	330710	40.00000	0.00012095

7 DELTA BHC Ret. Time = 20.35 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	60781	5.00000	0.00008226
2	125462	10.00000	0.00007971
3	244734	20.00000	0.00008172
4	377399	40.00000	0.00010599
5	926233	80.00000	0.00008637

8 ALDRIN(RP) Ret. Time = 21.33 min. Fit.type = 2
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%
AREA/AREA(int) = 1.0000D+00 * AMT/AMT(int) + 0.0000D+00
Correlation (R squared) = 1.0000

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	206237	20.00000	0.00009698
2	215565	20.00000	0.00009278
3	221246	20.00000	0.00009040
4	179642	20.00000	0.00011133
5	212646	20.00000	0.00009405

9 DACTHAL Ret. Time = 24.43 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	45810	5.00000	0.00010915
2	87332	10.00000	0.00011451
3	163393	20.00000	0.00012240
4	207027	40.00000	0.00019321
5	462746	80.00000	0.00017288

10 OXYCHLORDANE Ret. Time = 24.97 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	24428	2.50000	0.00010234
2	50730	5.00000	0.00009856
3	98320	10.00000	0.00010171
4	134998	20.00000	0.00014815
5	328993	40.00000	0.00012158

11 HEPTACHLOR EPOXIDE Ret. Time = 25.91 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	21092	2.50000	0.00011853
2	44515	5.00000	0.00011232
3	82940	10.00000	0.00012057
4	129743	20.00000	0.00015415
5	309133	40.00000	0.00012939

12 T-CHLORDANE Ret. Time = 27.45 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	27290	2.50000	0.00009161
2	54662	5.00000	0.00009147
3	107241	10.00000	0.00009325
4	166314	20.00000	0.00012025
5	389540	40.00000	0.00010269

13 T-NONACHLOR Ret. Time = 27.97 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	27603	2.50000	0.00009057
2	55853	5.00000	0.00008952
3	108248	10.00000	0.00009238
4	165538	20.00000	0.00012082
5	378062	40.00000	0.00010580

14 C-CHLORDANE Ret. Time = 28.80 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	28166	2.50000	0.00008876
2	57559	5.00000	0.00008687
3	110764	10.00000	0.00009028
4	175480	20.00000	0.00011397
5	414040	40.00000	0.00009661

15 o,p'-DDE Ret. Time = 29.19 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	31671	5.00000	0.00015787
2	63636	10.00000	0.00015714
3	121427	20.00000	0.00016471
4	186481	40.00000	0.00021450
5	419723	80.00000	0.00019060

16 DIELDRIN Ret. Time = 31.07 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	54628	5.00000	0.00009153
2	91821	10.00000	0.00010891
3	180834	20.00000	0.00011060
4	275995	40.00000	0.00014493
5	728665	80.00000	0.00010979

17 p,p'-DDE Ret. Time = 31.63 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	66815	5.00000	0.00007483
2	134232	10.00000	0.00007450
3	260528	20.00000	0.00007677
4	400945	40.00000	0.00009976
5	931075	80.00000	0.00008592

18 o,p'-DDD Ret. Time = 33.44 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	22679	5.00000	0.00022047
2	42486	10.00000	0.00023537
3	78063	20.00000	0.00025620
4	117128	40.00000	0.00034151
5	259122	80.00000	0.00030873

19 ENDRIN Ret. Time = 33.73 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	67794	10.00000	0.00014751
2	141974	20.00000	0.00014087
3	281882	40.00000	0.00014190
4	421620	80.00000	0.00018974
5	1001494	160.00000	0.00015976

20 C-NONACHLOR Ret. Time = 34.89 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	57474	5.00000	0.00008700
2	118182	10.00000	0.00008462
3	232302	20.00000	0.00008609
4	359709	40.00000	0.00011120
5	832846	80.00000	0.00009606

21 o,p'-DDT Ret. Time = 35.83 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	23008	5.00000	0.00021732
2	46002	10.00000	0.00021738
3	86000	20.00000	0.00023256
4	128244	40.00000	0.00031191
5	269962	80.00000	0.00029634

22 p,p'-DDD Ret. Time = 36.43 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	39838	10.00000	0.00025101
2	83496	20.00000	0.00023953
3	156377	40.00000	0.00025579
4	218233	80.00000	0.00036658
5	514282	160.00000	0.00031111

23 p,p'-DDT Ret. Time = 38.85 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	41258	10.00000	0.00024238
2	80702	20.00000	0.00024783
3	151699	40.00000	0.00026368
4	239233	80.00000	0.00033440
5	510975	160.00000	0.00031313

24 MIREX Ret. Time = 44.72 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

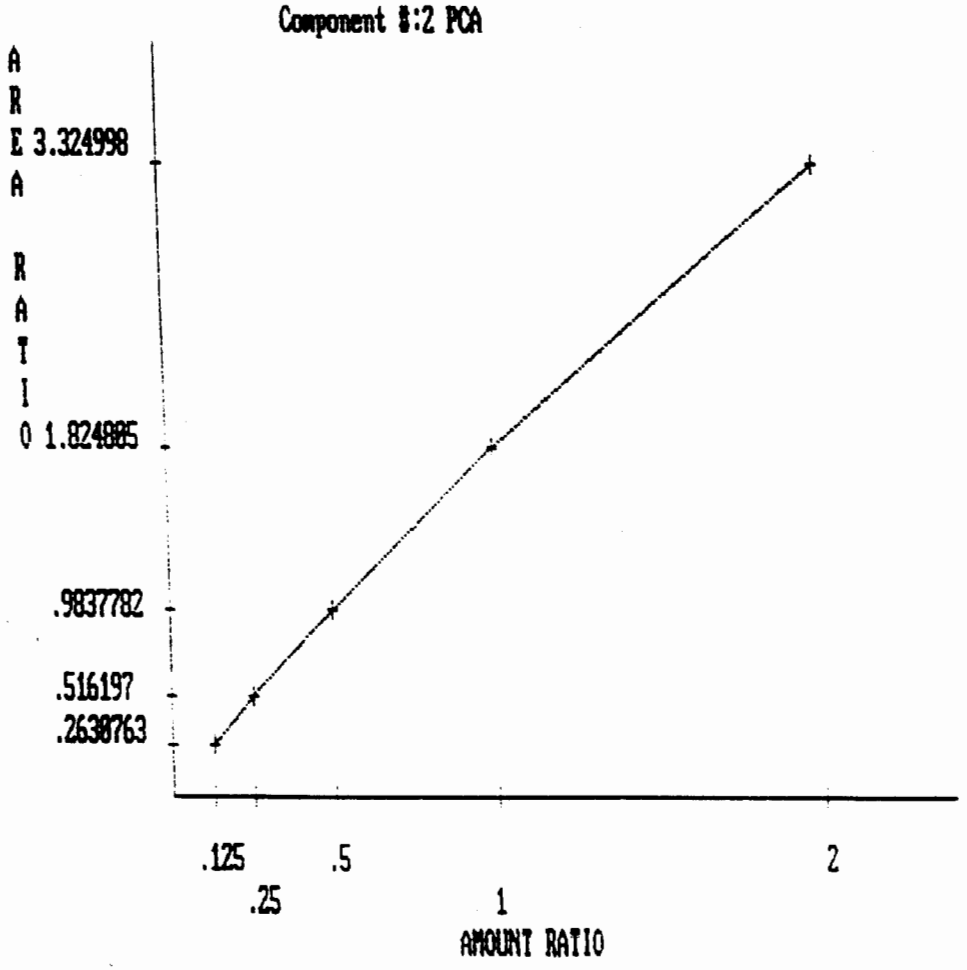
LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	115406	10.00000	0.00008665
2	231706	20.00000	0.00008632
3	428134	40.00000	0.00009343
4	638915	80.00000	0.00012521
5	1324153	160.00000	0.00012083

25 METHOXYCHLOR Ret. Time = 46.51 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.2%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	24654	12.50000	0.00050701
2	50256	25.00000	0.00049745
3	95288	50.00000	0.00052473
4	146162	100.00000	0.00068417
5	297001	200.00000	0.00067340

Ev#	Time	Event	Description
1	12.96	PD-	Peak Detection (on/off)
2	16.84	NEG+	Negative Peak Detection (on/off)
3	17.60	NEG-	Negative Peak Detection (on/off)
4	17.64	NEG+	Negative Peak Detection (on/off)
5	19.76	NEG-	Negative Peak Detection (on/off)
6	19.89	NEG+	Negative Peak Detection (on/off)

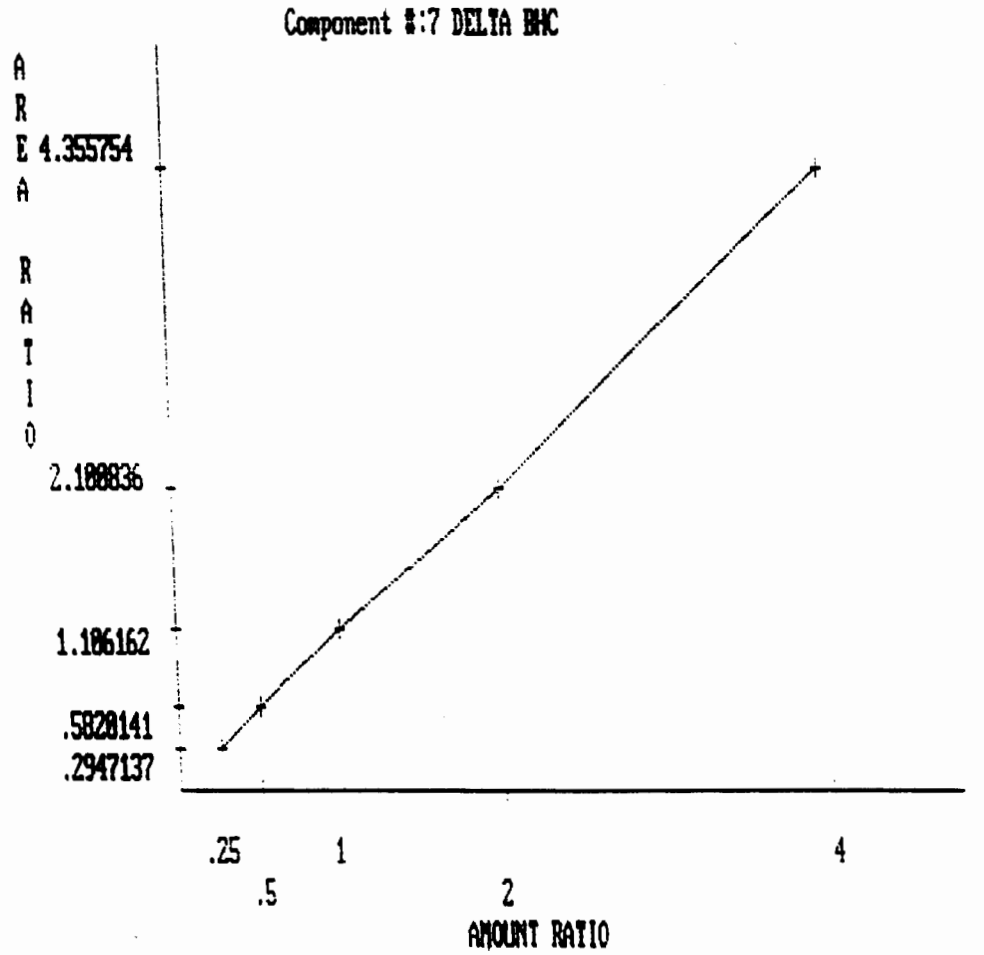
Method G:H14EY9
Sample Missouri River SPMD PRoject- ENV Chem
Operator CEOrazio
Run date 07-20-1993 15:38:44 version: 501
Printed on 09-13-1993 AT 10:47:05
Point-to-Point Fit



Component 2 = PCA
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	2.5000	54256	0.1250	0.2631
2	5.0000	111274	0.2500	0.5162
3	10.0000	217657	0.5000	0.9838
4	20.0000	327812	1.0000	1.8248
5	40.0000	707047	2.0000	3.3250

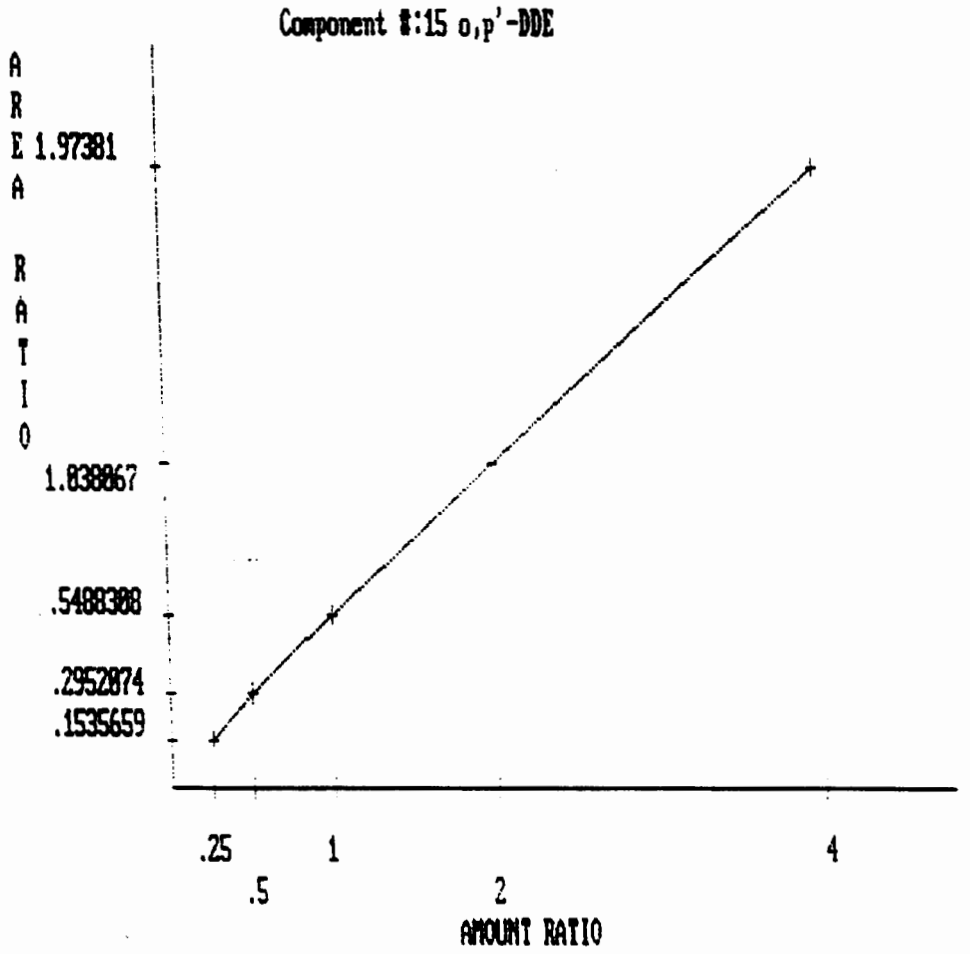
Method G:H14EY9
Sample Missouri River SPMD PRoject- ENV Chem
Operator CEOrazio
Run date 07-20-1993 15:38:44 version: 501
Printed on 09-13-1993 AT 10:47:30
Point-to-Point Fit



Component 7 = DELTA BHC
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	5.0000	60781	0.2500	0.2947
2	10.0000	125462	0.5000	0.5820
3	20.0000	244734	1.0000	1.1062
4	40.0000	377399	2.0000	2.1008
5	80.0000	926233	4.0000	4.3558

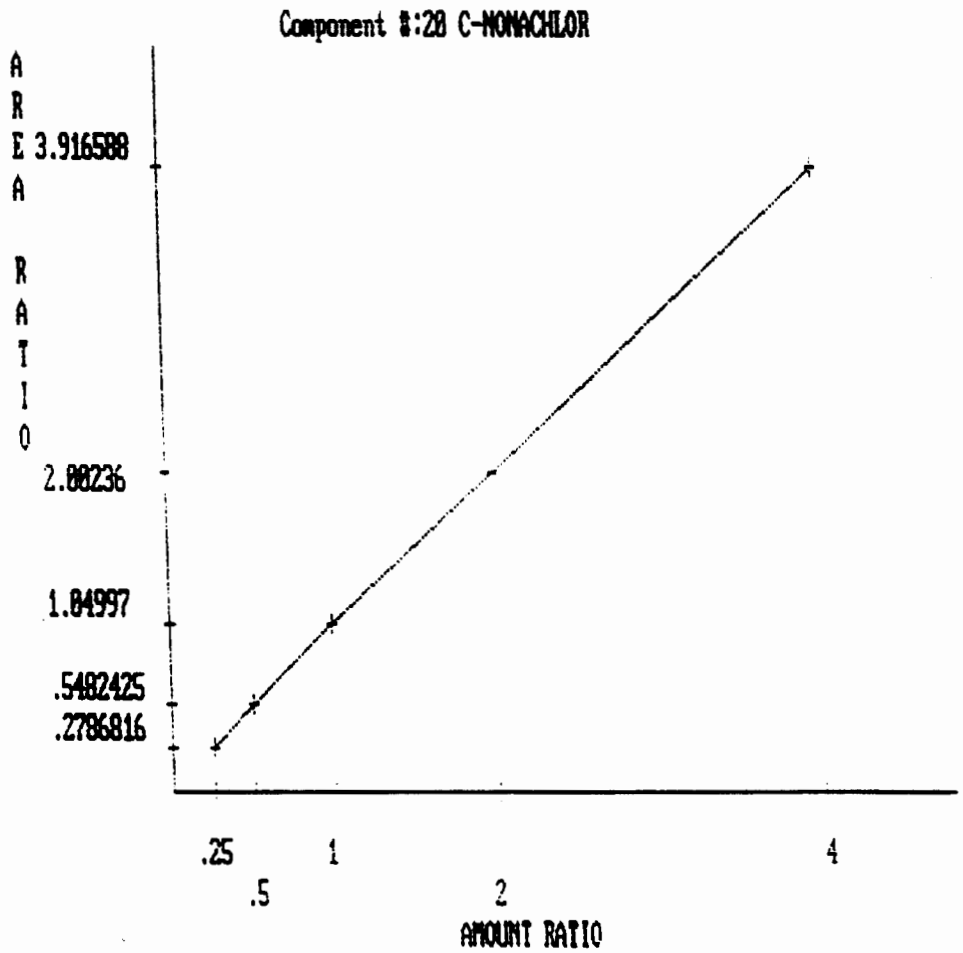
Method G:H14EY9
Sample Missouri River SPMD PRoject- ENV Chem
Operator CEOrazio
Run date 07-20-1993 15:38:44 version: 501
Printed on 09-13-1993 AT 10:48:23
Point-to-Point Fit



Component 15 = o,p'-DDE
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	5.0000	31671	0.2500	0.1536
2	10.0000	63636	0.5000	0.2952
3	20.0000	121427	1.0000	0.5488
4	40.0000	186481	2.0000	1.0381
5	80.0000	419723	4.0000	1.9738

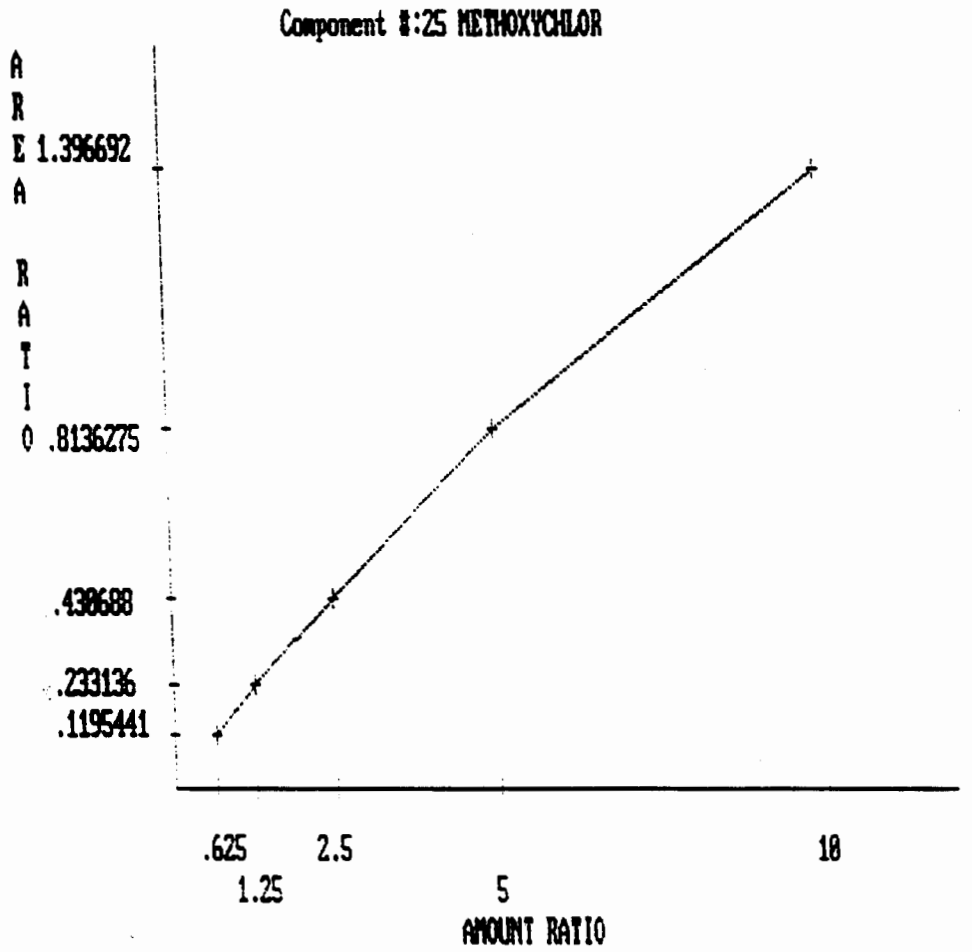
Method G:H14EY9
Sample Missouri River SPMD PRoject- ENV Chem
Operator CEOrazio
Run date 07-20-1993 15:38:44 version: 501
Printed on 09-13-1993 AT 10:48:50
Point-to-Point Fit



Component 20 = C-NONACHLOR
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	5.0000	57474	0.2500	0.2787
2	10.0000	118182	0.5000	0.5482
3	20.0000	232302	1.0000	1.0500
4	40.0000	359709	2.0000	2.0024
5	80.0000	832846	4.0000	3.9166

Method G:H14EY9
Sample Missouri River SPMD PRoject- ENV Chem
Operator CEOrazio
Run date 07-20-1993 15:38:44 version: 501
Printed on 09-13-1993 AT 10:49:14
Point-to-Point Fit



Component 25 = METHOXYCHLOR
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	12.5000	24654	0.6250	0.1195
2	25.0000	50256	1.2500	0.2331
3	50.0000	95288	2.5000	0.4307
4	100.0000	146162	5.0000	0.8136
5	200.0000	297001	10.0000	1.3967

Method file name: H:H12PP1
Default Sample Name: MoRiver SPMDs SG-1 fraction
Operator: CEORAZIO Date-time: 07-22-1993 16:10:32 version: 527

ACQUISITION PARAMETERS

SINGLE OR DUAL CHANNEL (1 OR 2)	1.00
RUN TIME (minutes)	58.00
END TIME FOR PLOTS (default=RUN TIME)	58.00
SOLVENT DELAY TIME (minutes)	0.00
PEAK DETECTION THRESHOLD (microv/sec)	1.00
Area Threshold	100.00
MINIMUM PEAK WIDTH (seconds)	10.00
TIME FOR ONE SAMPLE (seconds)	0.70
NUMBER OF REAL TIME CRT PAGES TO PLOT (0 TO 99)	1.00
REAL TIME PLOT FULL SCALE FOR CH.0 (millivolts)	100.00
REAL TIME FULL SCALE FOR CH.1 (millivolts)	200.00
HARD COPY REAL TIME PLOT	YES
AUTO ZERO REAL TIME PLOT	NO
Pre Version 4 method	YES
RECORD AREA TABLES ON DISK	NO
RECORD RAW DATA	YES
NUMBER OF CRT PAGES FOR REPLOT (1 TO 99)	0.00
VERTICAL SCALE FACTOR FOR REPLOT (units of largest peak)	4.00
OFFSET FOR THE REPLOT (millivolts)	0.00
PUT NAMES ON REPLOT?	NO
PRINT AREA PERCENT REPORT	NO
PRINT EXTERNAL STANDARD REPORT	NO
PRINT INTERNAL STANDARD REPORT	YES
FINAL REPORT AREA REJECT (microvolt-sec)	2500.00
LINK TO USER PROGRAM	NO
FORCE DROP LINE INTEGRATION	NO
FORCE COMMON BASE LINE	NO
FULL SCALE RANGE FOR A.D.C. (3=1VOLT, 1=2VOLT, 0=10VOLT)	3.00
AREA REJECT FOR REFERENCE PEAKS?	10000.00
% RET TIME WINDOW FOR REFERENCE PEAKS	0.30
RET TIME WINDOW IN SECONDS FOR REF. PEAKS	3.00
AREA OR PEAK HEIGHT QUANTITATION (0 OR 1)	0.00
PRINT GROUP REPORT	NO
NUMBER OF CALIBRATION LEVELS (1 TO 6)	5.00
LIST COMPONENTS NOT FOUND IN SAMPLE?	YES
INCLUDE UNKNOWN PEAKS IN REPORTS?	NO
UPDATE RESPONSE FACTORS WITH REPLACEMENT (0) OR AVERAGE (1)	1.00
DEFAULT DILUTION FACTOR	1.00
DEFAULT SAMPLE WEIGHT	1.00
DEFAULT AMOUNT INJECTED	1.00
DEFAULT AMOUNT OF INTERNAL STANDARD	20.00
PRINT GPC MW DISTRIBUTION	NO
PRINT SIMULATED DISTILLATION REPORT	NO

SAVE RAW DATA IN: H:H12PP.PTS
Response factor for unknowns= 1.0000E-04
Component Units = ng/smpl

1 a-BHC Ret. Time = 14.57 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.5%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	14604	2.50000	0.00017118
2	28221	5.00000	0.00017717
3	55871	10.00000	0.00017898
4	105335	20.00000	0.00018987
5	221398	40.00000	0.00018067

2 HCB Ret. Time = 14.85 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.5%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	60279	2.50000	0.00004147
2	121624	5.00000	0.00004111
3	241063	10.00000	0.00004148
4	433823	20.00000	0.00004610
5	824533	40.00000	0.00004851

3 PCAnisole Ret. Time = 15.20 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.5%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	48915	2.50000	0.00005111
2	104210	5.00000	0.00004798
3	214814	10.00000	0.00004655
4	401145	20.00000	0.00004986
5	769962	40.00000	0.00005195

4 Lindane Ret. Time = 16.21 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.5%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	86964	2.50000	0.00002875
2	175008	5.00000	0.00002857
3	350808	10.00000	0.00002851
4	574011	20.00000	0.00003484
5	1071357	40.00000	0.00003734

5 B-BHC Ret. Time = 16.35 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.5%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	22110	5.00000	0.00022614
2	41883	10.00000	0.00023876
3	59856	20.00000	0.00033414
4	142210	40.00000	0.00028128
5	250843	80.00000	0.00031892

6 DELTA-BHC Ret. Time = 18.20 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.5%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	51819	10.00000	0.00019298
2	105280	20.00000	0.00018997
3	221339	40.00000	0.00018072
4	421999	80.00000	0.00018957
5	848530	160.00000	0.00018856

7 HEPTACHLOR Ret. Time = 20.94 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.5%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	23920	2.50000	0.00010451
2	45791	5.00000	0.00010919
3	87427	10.00000	0.00011438
4	157211	20.00000	0.00012722
5	309459	40.00000	0.00012926

8 ALDRIN(RP) Ret. Time = 23.30 min. Fit.type = 2
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%
AREA/AREA(int) = 1.0000D+00 * AMT/AMT(int) + 0.0000D+00
Correlation (R squared) = 1.0000

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	142157	20.00000	0.00014069
2	145475	20.00000	0.00013748
3	154497	20.00000	0.00012945
4	150528	20.00000	0.00013287
5	157248	20.00000	0.00012719

9 DACTHAL Ret. Time = 25.11 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	58153	5.00000	0.00008598
2	102018	10.00000	0.00009802
3	163700	20.00000	0.00012217
4	349510	40.00000	0.00011445
5	575511	80.00000	0.00013901

10 OXY & Heptepox Ret. Time = 26.55 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	37184	2.50000	0.00006723
2	72743	5.00000	0.00006874
3	138054	10.00000	0.00007244
4	252149	20.00000	0.00007932
5	494358	40.00000	0.00008091

11 t-chlordane Ret. Time = 28.50 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	22778	2.50000	0.00010976
2	43464	5.00000	0.00011504
3	83460	10.00000	0.00011982
4	152132	20.00000	0.00013147
5	303863	40.00000	0.00013164

12 op-DDE Ret. Time = 29.49 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	29317	5.00000	0.00017055
2	57005	10.00000	0.00017542
3	114947	20.00000	0.00017399
4	215362	40.00000	0.00018573
5	430365	80.00000	0.00018589

13 c-chlordane Ret. Time = 29.75 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	23449	2.50000	0.00010662
2	43771	5.00000	0.00011423
3	84255	10.00000	0.00011869
4	154316	20.00000	0.00012960
5	306748	40.00000	0.00013040

14 t-nonachlor Ret. Time = 30.14 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	23305	2.50000	0.00010727
2	44389	5.00000	0.00011264
3	84054	10.00000	0.00011897
4	152523	20.00000	0.00013113
5	298782	40.00000	0.00013388

15 Dieldrin Ret. Time = 31.26 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	33989	5.00000	0.00014711
2	65160	10.00000	0.00015347
3	131119	20.00000	0.00015253
4	249910	40.00000	0.00016006
5	516058	80.00000	0.00015502

16 pp-DDE Ret. Time = 32.24 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	63206	10.00000	0.00015821
2	133442	20.00000	0.00014988
3	289937	40.00000	0.00013796
4	559059	80.00000	0.00014310
5	1124216	160.00000	0.00014232

17 op-DDD Ret. Time = 32.83 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	22199	5.00000	0.00022523
2	43341	10.00000	0.00023073
3	82387	20.00000	0.00024276
4	150625	40.00000	0.00026556
5	286804	80.00000	0.00027894

18 ENDRIN Ret. Time = 33.10 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	53145	10.00000	0.00018817
2	107524	20.00000	0.00018601
3	214547	40.00000	0.00018644
4	402392	80.00000	0.00019881
5	795465	160.00000	0.00020114

19 pp-DDD Ret. Time = 35.26 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	43618	10.00000	0.00022926
2	83322	20.00000	0.00024003
3	163121	40.00000	0.00024522
4	307251	80.00000	0.00026037
5	615537	160.00000	0.00025994

20 op-ddt & c-nonaclr Ret. Time = 35.81 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	62490	10.00000	0.00016003
2	122928	20.00000	0.00016270
3	240998	40.00000	0.00016598
4	452252	80.00000	0.00017689
5	871377	160.00000	0.00018362

21 pp-DDT Ret. Time = 38.86 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	48196	10.00000	0.00020748
2	92714	20.00000	0.00021572
3	180752	40.00000	0.00022130
4	339498	80.00000	0.00023564
5	666732	160.00000	0.00023998

22 Methoxychlor Ret. Time = 44.26 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

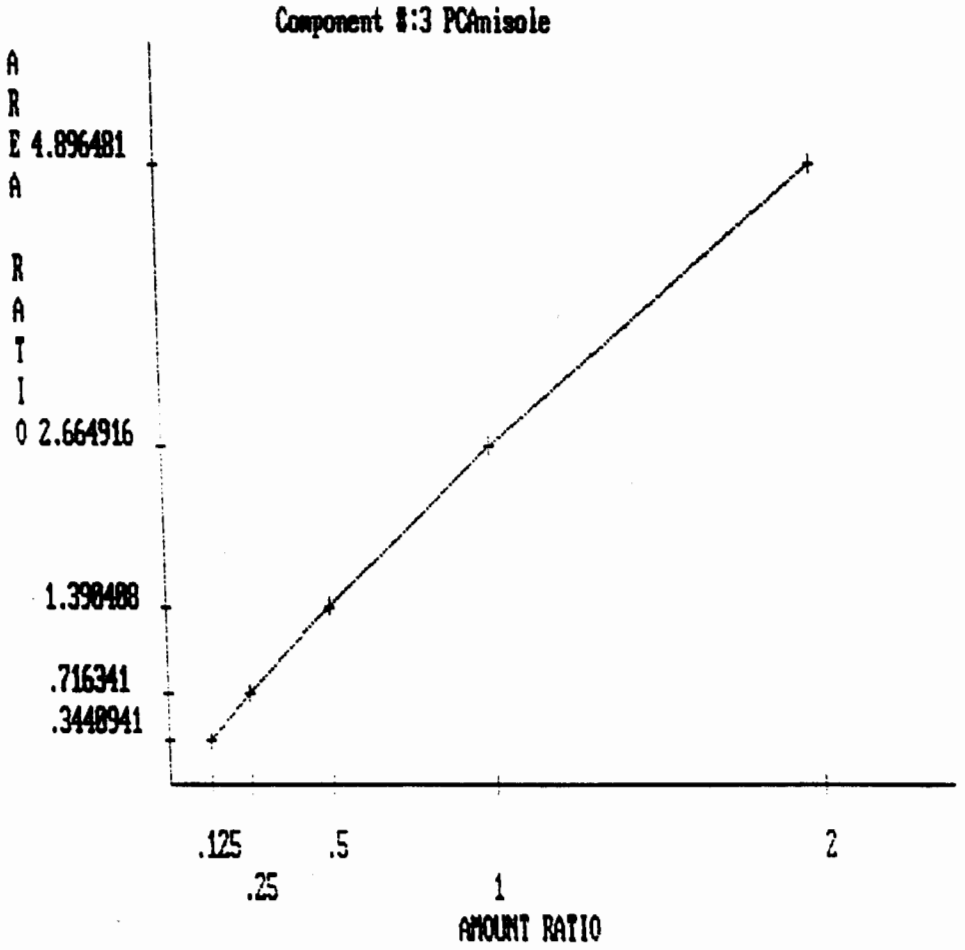
LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	36008	12.50000	0.00034714
2	69386	25.00000	0.00036030
3	130373	50.00000	0.00038352
4	233943	100.00000	0.00042746
5	436301	200.00000	0.00045840

23 MIREX Ret. Time = 45.71 min. Fit.type = 0
Ref. peak: ALDRIN(RP) Int Std: ALDRIN(RP) Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	76595	10.00000	0.00013056
2	141918	20.00000	0.00014093
3	264016	40.00000	0.00015151
4	460703	80.00000	0.00017365
5	847493	160.00000	0.00018879

Ev#	Time	Event	Description
1	0.00	PD-	Peak Detection (on/off)
2	13.91	PD+	Peak Detection (on/off)
3	30.40	NEG-	Negative Peak Detection (on/off)

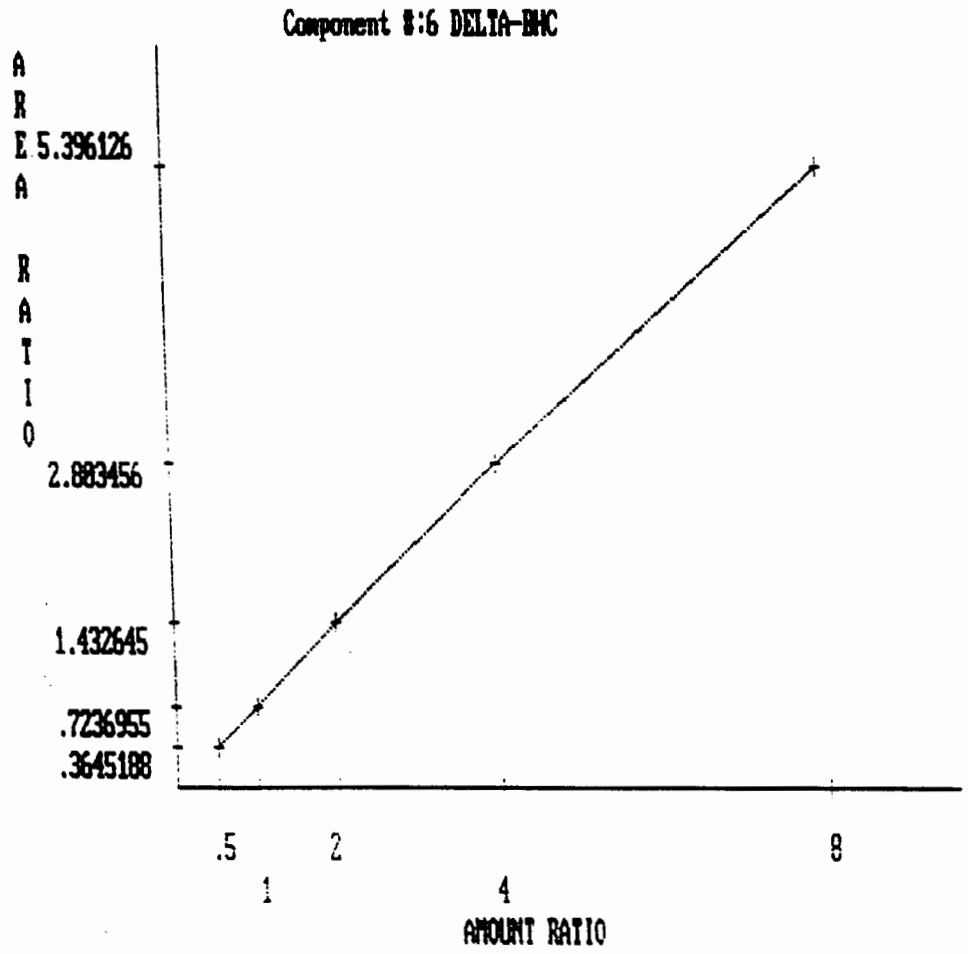
Method H:H12PP1
Sample MoRiver SPMDs SG-1 fraction
Operator CEORAZIO
Run date 07-22-1993 16:10:32 version: 527
Printed on 09-13-1993 AT 10:51:31
Point-to-Point Fit



Component 3 = PCAnisole
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	2.5000	48915	0.1250	0.3441
2	5.0000	104210	0.2500	0.7163
3	10.0000	214814	0.5000	1.3904
4	20.0000	401145	1.0000	2.6649
5	40.0000	769962	2.0000	4.8965

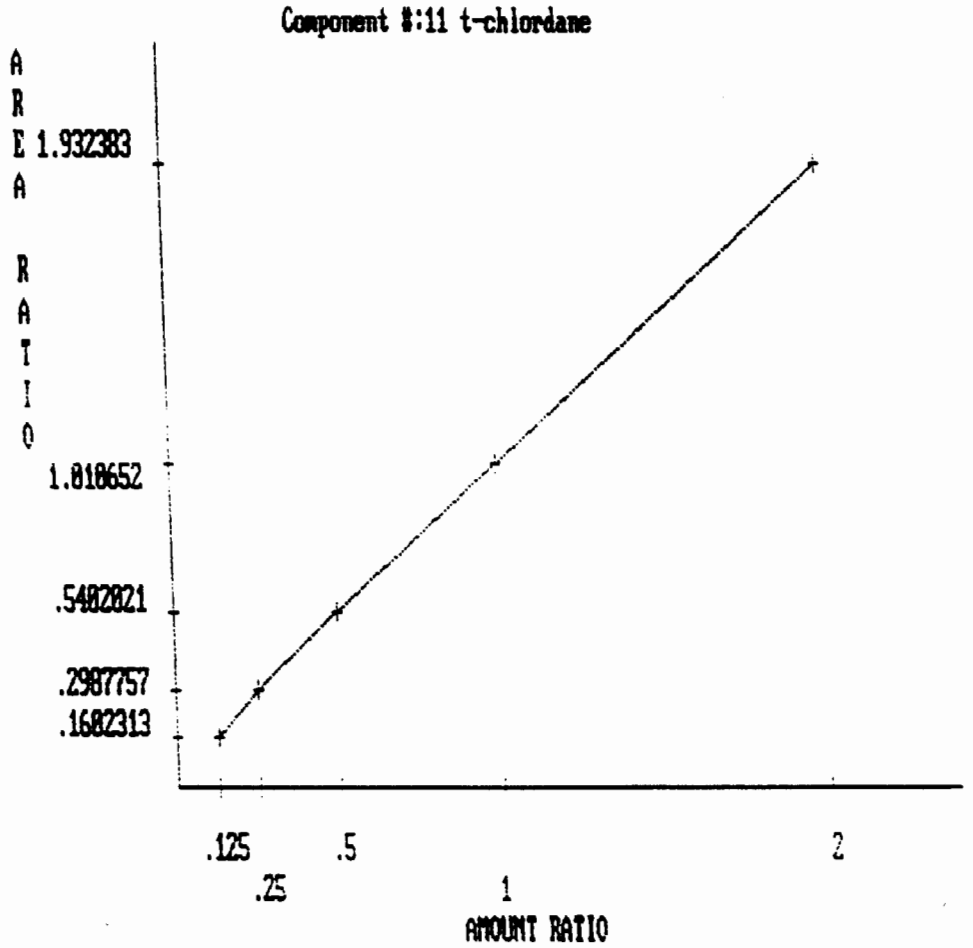
Method H:H12PP1
Sample MoRiver SPMDs SG-1 fraction
Operator CEORAZIO
Run date 07-22-1993 16:10:32 version: 527
Printed on 09-13-1993 AT 10:52:54
Point-to-Point Fit



Component 6 = DELTA-BHC
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	10.0000	51819	0.5000	0.3645
2	20.0000	105280	1.0000	0.7237
3	40.0000	221339	2.0000	1.4326
4	80.0000	421999	4.0000	2.8035
5	160.0000	848530	8.0000	5.3961

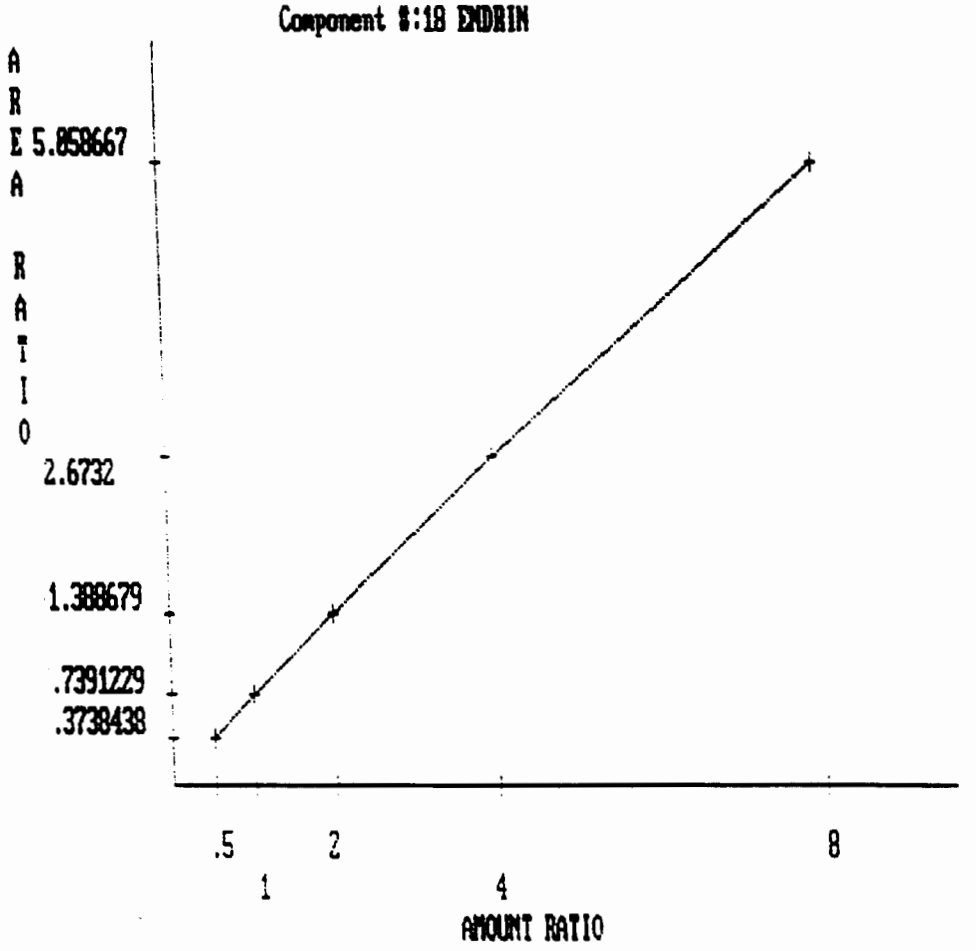
Method H:H12PP1
Sample MoRiver SPMDs SG-1 fraction
Operator CEORAZIO
Run date 07-22-1993 16:10:32 version: 527
Printed on 09-13-1993 AT 10:53:50
Point-to-Point Fit



Component 11 = t-chlordane
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	2.5000	22778	0.1250	0.1602
2	5.0000	43464	0.2500	0.2988
3	10.0000	83460	0.5000	0.5402
4	20.0000	152132	1.0000	1.0107
5	40.0000	303863	2.0000	1.9324

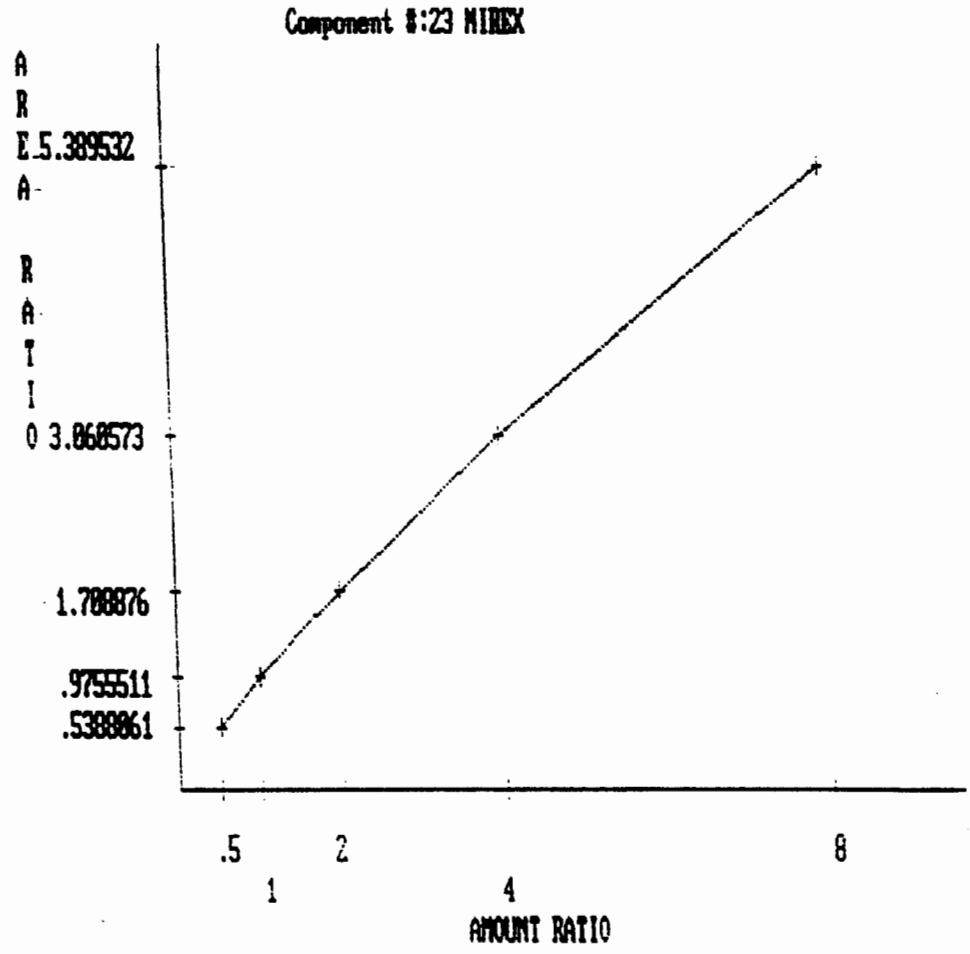
Method H:H12PP1
Sample MoRiver SPMDs SG-1 fraction
Operator CEORAZIO
Run date 07-22-1993 16:10:32 version: 527
Printed on 09-13-1993 AT 10:54:45
Point-to-Point Fit



Component 18 = ENDRIN
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	10.0000	53145	0.5000	0.3738
2	20.0000	107524	1.0000	0.7391
3	40.0000	214547	2.0000	1.3887
4	80.0000	402392	4.0000	2.6732
5	160.0000	795465	8.0000	5.0587

Method H:H12PP1
Sample MoRiver SPMDs SG-1 fraction
Operator CEORAZIO
Run date 07-22-1993 16:10:32 version: 527
Printed on 09-13-1993 AT 10:55:51
Point-to-Point Fit



Component 23 = MIREX
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	10.0000	76595	0.5000	0.5388
2	20.0000	141918	1.0000	0.9756
3	40.0000	264016	2.0000	1.7089
4	80.0000	460703	4.0000	3.0606
5	160.0000	847493	8.0000	5.3895

Method file name: H:H12PPAH
Default Sample Name: Missouri River SPMD Project- EnvChemGrp
Operator: CEOrazio
Date-time: 05-24-1993 15:49:25 version: 231

ACQUISITION PARAMETERS

SINGLE OR DUAL CHANNEL (1 OR 2)	1.00
RUN TIME (minutes)	64.00
END TIME FOR PLOTS (default=RUN TIME)	64.00
SOLVENT DELAY TIME (minutes)	0.00
PEAK DETECTION THRESHOLD (microv/sec)	1.00
Area Threshold	100.00
MINIMUM PEAK WIDTH (seconds)	10.00
TIME FOR ONE SAMPLE (seconds)	0.70
NUMBER OF REAL TIME CRT PAGES TO PLOT (0 TO 99)	1.00
REAL TIME PLOT FULL SCALE FOR CH.0 (millivolts)	50.00
REAL TIME FULL SCALE FOR CH.1 (millivolts)	200.00
HARD COPY REAL TIME PLOT	YES
AUTO ZERO REAL TIME PLOT	NO
Pre Version 4 method	YES
RECORD AREA TABLES ON DISK	NO
RECORD RAW DATA	YES
NUMBER OF CRT PAGES FOR REPLOT (1 TO 99)	0.00
VERTICAL SCALE FACTOR FOR REPLOT (units of largest peak)	4.00
OFFSET FOR THE REPLOT (millivolts)	0.00
PUT NAMES ON REPLOT?	YES
PRINT AREA PERCENT REPORT	NO
PRINT EXTERNAL STANDARD REPORT	NO
PRINT INTERNAL STANDARD REPORT	YES
FINAL REPORT AREA REJECT (microvolt-sec)	750.00
LINK TO USER PROGRAM	NO
FORCE DROP LINE INTEGRATION	NO
FORCE COMMON BASE LINE	NO
FULL SCALE RANGE FOR A.D.C. (3=1VOLT, 1=2VOLT, 0=10VOLT)	0.00
AREA REJECT FOR REFERENCE PEAKS?	30000.00
% RET TIME WINDOW FOR REFERENCE PEAKS	0.50
RET TIME WINDOW IN SECONDS FOR REF. PEAKS	2.00
AREA OR PEAK HEIGHT QUANTITATION (0 OR 1)	0.00
PRINT GROUP REPORT	NO
NUMBER OF CALIBRATION LEVELS (1 TO 6)	5.00
LIST COMPONENTS NOT FOUND IN SAMPLE?	YES
INCLUDE UNKNOWN PEAKS IN REPORTS?	NO
UPDATE RESPONSE FACTORS WITH REPLACEMENT (0) OR AVERAGE (1)	0.00
DEFAULT DILUTION FACTOR	1.00
DEFAULT SAMPLE WEIGHT	1.00
DEFAULT AMOUNT INJECTED	1.00
DEFAULT AMOUNT OF INTERNAL STANDARD	4.00
PRINT GPC MW DISTRIBUTION	NO
PRINT SIMULATED DISTILLATION REPORT	NO

SAVE RAW DATA IN: H:H12HZ.PTS
Response factor for unknowns= 1.0000E-04
Component Units = ug/site

1 naphthalene Ret. Time = 5.77 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.9%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	4855	0.20000	0.00004120
2	11291	0.50000	0.00004428
3	51457	2.00000	0.00003887
4	108808	4.00000	0.00003676
5	226689	8.00000	0.00003529

2 *azulene-IStd Ret. Time = 8.37 min. Fit.type = 2
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.5%
AREA/AREA(int) = 1.0000D+00 * AMT/AMT(int) + 0.0000D+00
Correlation (R squared) = 1.0000

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	129557	4.00000	0.00003087
2	115229	4.00000	0.00003471
3	118054	4.00000	0.00003388
4	122107	4.00000	0.00003276
5	128458	4.00000	0.00003114

3 acenaphthalene Ret. Time = 12.30 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.7%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	3482	0.20000	0.00005744
2	8889	0.50000	0.00005625
3	41819	2.00000	0.00004783
4	90871	4.00000	0.00004402
5	199022	8.00000	0.00004020

4 acenaphthene Ret. Time = 13.41 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.7%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	4969	0.20000	0.00004025
2	12153	0.50000	0.00004114
3	57438	2.00000	0.00003482
4	127394	4.00000	0.00003140
5	279667	8.00000	0.00002861

5 fluorene Ret. Time = 16.61 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.6%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	3533	0.20000	0.00005661
2	8412	0.50000	0.00005944
3	36934	2.00000	0.00005415
4	84308	4.00000	0.00004745
5	189352	8.00000	0.00004225

6 phenanthrene Ret. Time = 23.16 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.6%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	4347	0.20000	0.00004601
2	10346	0.50000	0.00004833
3	44309	2.00000	0.00004514
4	92023	4.00000	0.00004347
5	193219	8.00000	0.00004140

7 anthracene Ret. Time = 23.48 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.9%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	3365	0.20000	0.00005943
2	8268	0.50000	0.00006047
3	41049	2.00000	0.00004872
4	91428	4.00000	0.00004375
5	213124	8.00000	0.00003754

8 fluoranthene Ret. Time = 32.19 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.9%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	2938	0.20000	0.00006807
2	7112	0.50000	0.00007031
3	31305	2.00000	0.00006389
4	66855	4.00000	0.00005983
5	142593	8.00000	0.00005610

9 pyrene Ret. Time = 33.71 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.7%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	2429	0.20000	0.00008234
2	6094	0.50000	0.00008205
3	28137	2.00000	0.00007108
4	59148	4.00000	0.00006763
5	124419	8.00000	0.00006430

10 benzo(a)anthracene Ret. Time = 43.42 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.9%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	3704	0.20000	0.00005399
2	9129	0.50000	0.00005477
3	39897	2.00000	0.00005013
4	83815	4.00000	0.00004772
5	176640	8.00000	0.00004529

11 chrysene Ret. Time = 43.70 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.9%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	2728	0.20000	0.00007331
2	6697	0.50000	0.00007466
3	30939	2.00000	0.00006464
4	66714	4.00000	0.00005996
5	149891	8.00000	0.00005337

12 bz(b)fluoranthene Ret. Time = 51.39 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	3326	0.20000	0.00006013
2	8192	0.50000	0.00006103
3	34436	2.00000	0.00005808
4	70723	4.00000	0.00005656
5	147597	8.00000	0.00005420

13 bz(k)fluoranthene Ret. Time = 51.58 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.3%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	2504	0.20000	0.00007989
2	6174	0.50000	0.00008099
3	27299	2.00000	0.00007326
4	59308	4.00000	0.00006744
5	128719	8.00000	0.00006215

14 benzo(a)pyrene Ret. Time = 53.41 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.4%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	2520	0.20000	0.00007938
2	6426	0.50000	0.00007780
3	28558	2.00000	0.00007003
4	61036	4.00000	0.00006554
5	127251	8.00000	0.00006287

15 inden(123cd)pyrene Ret. Time = 60.45 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.4%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	2326	0.20000	0.00008598
2	5934	0.50000	0.00008427
3	26306	2.00000	0.00007603
4	54500	4.00000	0.00007339
5	112997	8.00000	0.00007080

16 dibz(ah)anthracene Ret. Time = 60.84 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.4%

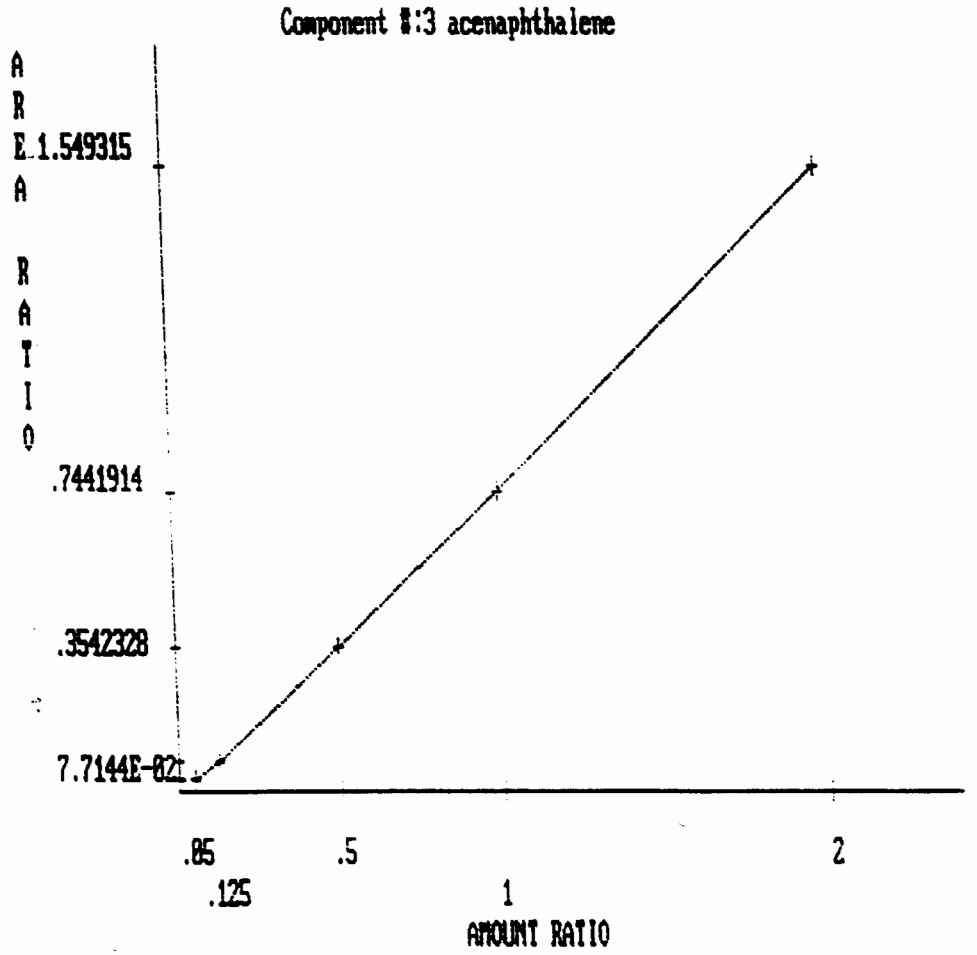
LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	3461	0.20000	0.00005778
2	8595	0.50000	0.00005818
3	38518	2.00000	0.00005192
4	81872	4.00000	0.00004886
5	177024	8.00000	0.00004519

17 benzo(ghi)perylene Ret. Time = 61.78 min. Fit.type = 0
Ref. peak: *azulene-IStd Int Std: *azulene-IStd Window size: 0.4%

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	2058	0.20000	0.00009718
2	5322	0.50000	0.00009395
3	23307	2.00000	0.00008581
4	48619	4.00000	0.00008227
5	102033	8.00000	0.00007841

Ev#	Time	Event	Description
1	0.01	PD-	Peak Detection (on/off)
2	5.00	PD+	Peak Detection (on/off)

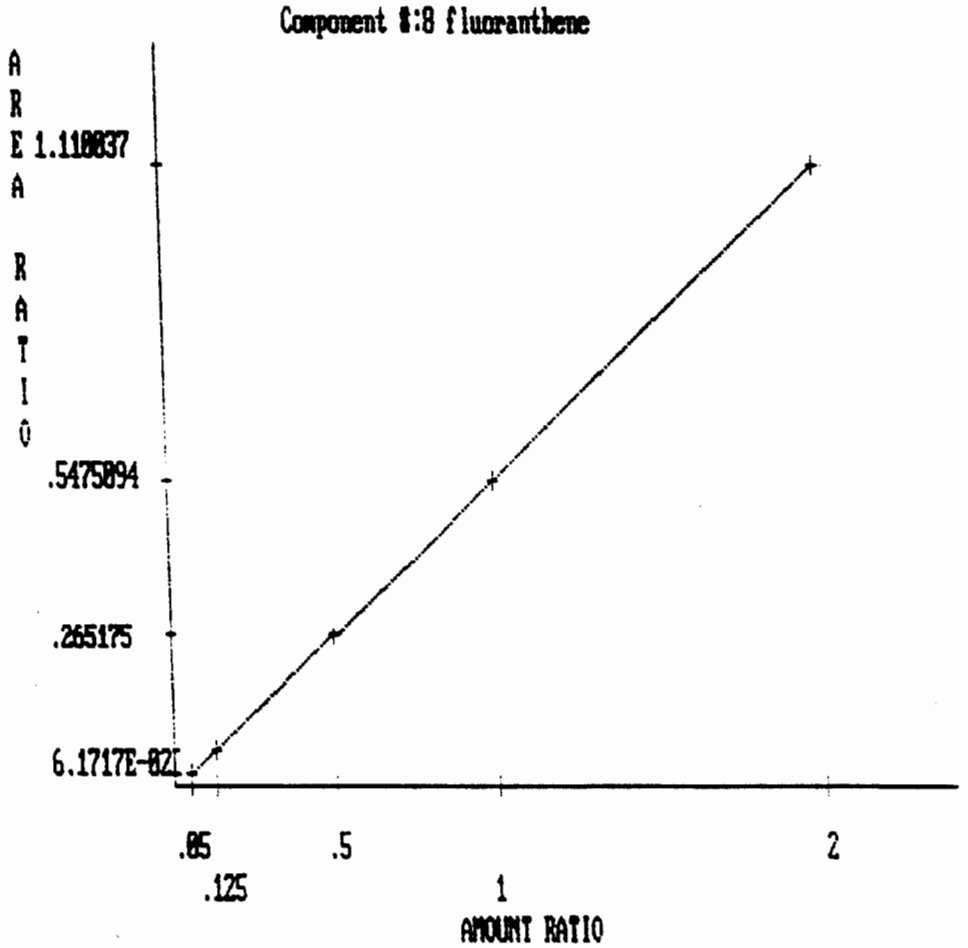
Method H:H12PPAH
Sample Missouri River SPMD Project- EnvChemGrp
Operator CEOrazio
Run date 05-24-1993 15:49:25 version: 231
Printed on 09-13-1993 AT 10:41:44
Point-to-Point Fit



Component 3 = acenaphthalene
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	0.2000	3482	0.0500	0.0269
2	0.5000	8889	0.1250	0.0771
3	2.0000	41819	0.5000	0.3542
4	4.0000	90871	1.0000	0.7442
5	8.0000	199022	2.0000	1.5493

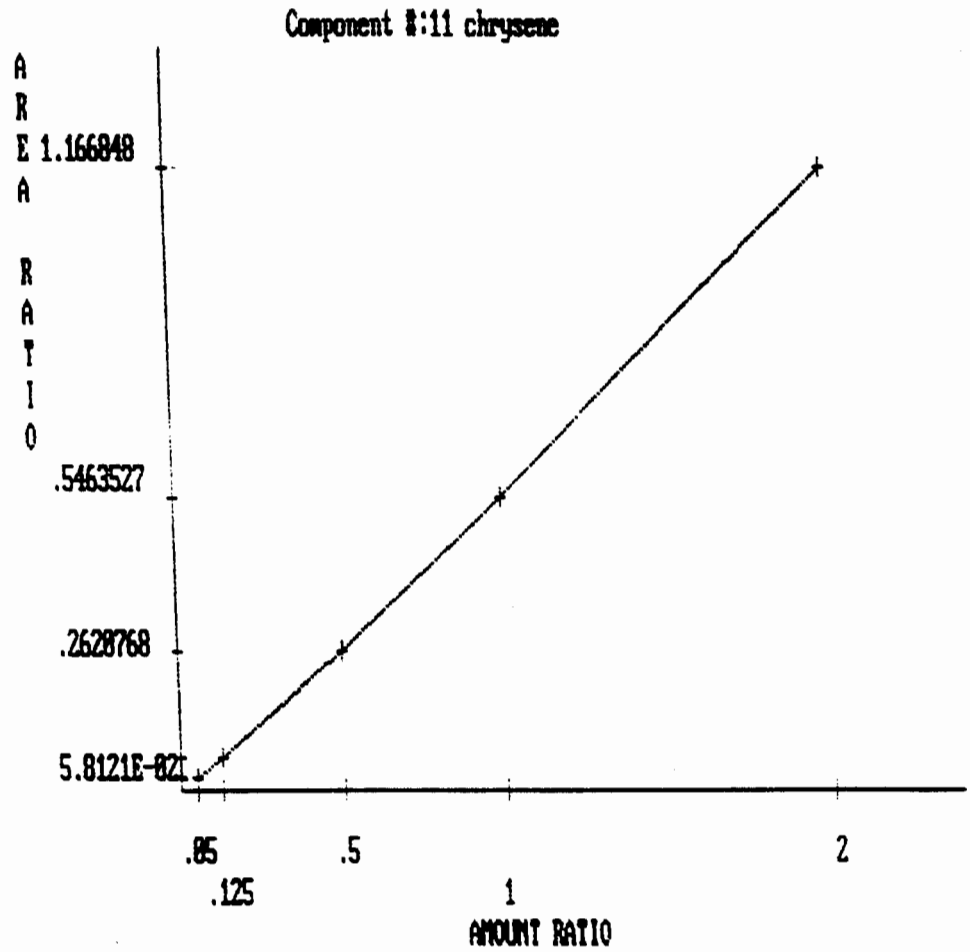
Method H:H12PPAH
Sample Missouri River SPMD Project- EnvChemGrp
Operator CEOrazio
Run date 05-24-1993 15:49:25 version: 231
Printed on 09-13-1993 AT 10:43:35
Point-to-Point Fit



Component 8 = fluoranthene
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	0.2000	2938	0.0500	0.0227
2	0.5000	7112	0.1250	0.0617
3	2.0000	31305	0.5000	0.2652
4	4.0000	66855	1.0000	0.5475
5	8.0000	142593	2.0000	1.1100

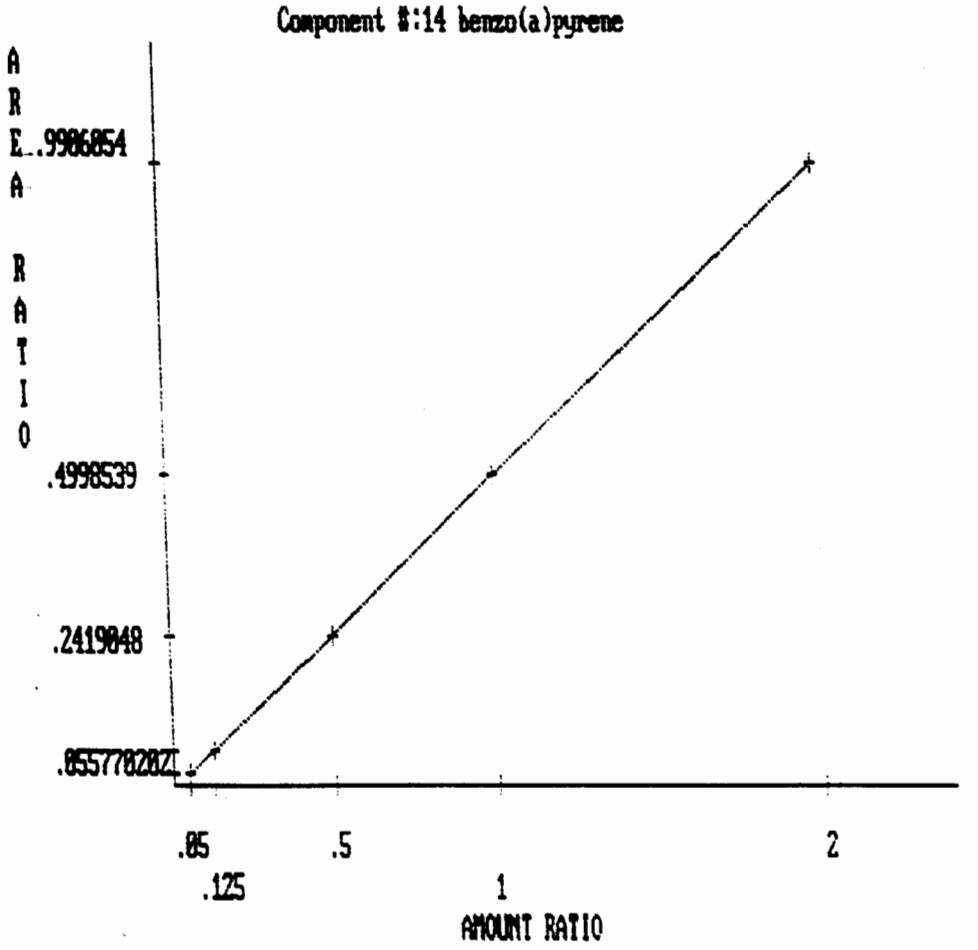
Method H:H12PPAH
Sample Missouri River SPMD Project- EnvChemGrp
Operator CEOrazio
Run date 05-24-1993 15:49:25 version: 231
Printed on 09-13-1993 AT 10:44:09
Point-to-Point Fit



Component 11 = chrysene
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	0.2000	2728	0.0500	0.0211
2	0.5000	6697	0.1250	0.0581
3	2.0000	30939	0.5000	0.2621
4	4.0000	66714	1.0000	0.5464
5	8.0000	149891	2.0000	1.1668

Method H:H12PPAH
Sample Missouri River SPMD Project- EnvChemGrp
Operator CEOrazio
Run date 05-24-1993 15:49:25 version: 231
Printed on 09-13-1993 AT 10:44:30
Point-to-Point Fit



Component 14 = benzo(a)pyrene
INTERNAL STANDARD CALIBRATION

LEVEL	AMOUNT	AREA	AMOUNT Ratio	AREA Ratio
1	0.2000	2520	0.0500	0.0194
2	0.5000	6426	0.1250	0.0558
3	2.0000	28558	0.5000	0.2419
4	4.0000	61036	1.0000	0.4999
5	8.0000	127251	2.0000	0.9906