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Sampling and Analysis of Selected Toxic Substances

Task 2: Analysis for Semivolatile Brominated Organics in Fish and Turtles

EPA-560/13-80-006

SAMPLING AND ANALYSIS OF SELECTED TOXIC SUBSTANCES
TASK 2: ANALYSIS FOR SEMIVOLATILE BROMINATED ORGANICS IN FISH AND TURTLES

by

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Task 2

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OFFICE OF PESTICIDES AND TOXIC SUBSTANCES
U. S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D. C. 20460

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ABSTRACT

Fish and turtle (5 from Arkansas and 3 from Louisiana) caught downstream of the brominated organic chemical industry near El Dorado, AR were extracted, cleaned up, and analyzed by GC/MS for brominated organics using full scan and single ion monitoring electron impact GC/MS, and negative ion chemical ionization GC/MS. PBBs ($C_{12}H_4Br_6$ and $C_{12}H_3Br_7$) were identified in one sample and several other brominated compounds were tentatively identified in several samples. Due to the high levels of interferences and very low levels of the compounds of interest, further identifications were impossible. The compounds were not quantitated, but levels appear to be much less than 1 ppm.

CONTENTS

FIGURES

TABLES

LIST OF ABBREVIATIONS

GC/EIMS	gas chromatography/electron impact mass spectrometry/computer
GC/ECD	gas chromatography with electron capture detection
GC/MS	gas chromatography/mass spectrometry/computer
GC/NICIMS	gas chromatography/negative ion chemical ionization mass spectrometry/computer
m/z	mass to charge ratio
SIM	Selected ion monitoring

ACKNOWLEDGEMENTS

The authors wish to thank Frank Hall and David Parrish, USEPA, Region VI, Dallas, Texas for arranging the sampling; John Geise of the Arkansas Department for Pollution Control and Ecology and Lewis Johnson of the Louisiana Department of Wildlife and Fisheries for conducting the sampling; Barbara Bickford, Pam Gentry, and Steve Burke for assistance with the GC/MS analysis, and Lynna Oglesby for typing the report. We also wish to acknowledge the Project Officers, Drs. Vincent DeCarlo and Thomas Kopp of OPTS, EPA, Washington, D.C. for their assistance.

SECTION 1
SUMMARY AND CONCLUSIONS

Hexabromobiphenyl and heptabromobiphenyl were identified in one sample (AR2 D010). Decabromobiphenyl ether was tentatively identified in four samples; decabromobiphenyl was tentatively identified in one sample; and one sample contained three unidentified brominated compounds. By comparison to the response of standards, all brominated compounds were present at much less than 1 ppm.

The analysis required the use of both positive ion and negative ion GC/MS. Analysis by GC/EIMS alone would have incorrectly identified several brominated compounds. Further development of the use of GC/NICIMS will facilitate better use of this technique in future analyses of this type.

The high background of these samples interfered significantly with the analysis, and forced the use of extra cleanup steps. Future analysis of this type should employ better cleanup techniques, possibly gel permeation chromatography.

SECTION 2
INTRODUCTION

Previous studies have shown the presence of brominated organics in the air, water, soil and other environmental media near the brominated organic manufacturing industries near El Dorado and Magnolia, AR.[1-3] It is of interest to determine if these chemicals are concentrating in and possibly migrating with aquatic organisms. The objective of this study was to analyze several fish and turtle samples collected "downstream" from the alleged sources near El Dorado, AR to see if brominated organics were present.

SECTION 3
RESULTS

SAMPLE RECEIPT

On July 13, 1979, five samples were received from Arkansas. On October 9, 1979 three samples were received from L.R.C. Johnson, Monroe, LA. The samples were collected from streams and rivers near brominated chemical manufacturing plants in the El Dorado, AR area. The samples consisted of turtles and fish and were composited by sampling personnel. The samples were received frozen in dry ice and were immediately transferred to a freezer awaiting analysis. The samples received are summarized in Table 1. Copies of the sample location map and "Field Data Sheets" are attached in Appendices A and B.

PREPARATION OF SAMPLES FOR ANALYSIS

The samples were allowed to thaw at room temperature for three hours, then they were placed in a refrigerator overnight. Approximately 100 g of each sample was weighed out for analysis (see Table 2). Fish samples AR2E021, AR2E018 and AR2E016 utilized several whole fish. Sample AR2D010 was a mixture of turtle organs which were placed in a blender and homogenized. Approximately 10% of the resulting macerate was used for analysis. Sample LA03 consisted of three large gars weighing more than 200 g each. One fish was homogenized in a blender and about one half of the macerate analyzed.

The samples were worked up using the analytical protocol in Appendix C. Specific details and deviations from the protocol are discussed below. The samples were extracted by placing them in a blender with 150 mL of redistilled hexane. The samples were broken up into small pieces using a slow blender setting (mince) for approximately 30 sec. Then, the mixture was blended at the highest blender speed (liquefy) for 30 sec. The macerate was scraped down the sides of the blender, followed by another 30 sec of the high speed blending. The hexane solution was decanted, and the solids were reextracted with 2 x 100 mL portions of fresh, redistilled hexane using the above extrac-

Table 1. SUMMARY OF SAMPLES RECEIVED FROM ARKANSAS AND LOUISIANA

Sample Code	Source of Sample	Sampling Date	Time	Sample Weight (lb)	Description
AR2D008	Bayou de Loutre	July 12, 1979	0940	[a]	common snapping turtle
AR2D010	Bayou de Loutre	July 11, 1979	0900	[a]	alligator and snapper turtles and (1) red ear slider
AR2E016	Cornie Bayou at Junction City	July 10, 1979	1000	2.1	fish: bullheads, sunfish and sucker
AR2E018	Bayou Cornie	July 11, 1979	1100	1.3	fish: bass, sunfish and crappie
AR2E021	Tributary of Cornie Bayou	July 10, 1979	1400	[a]	fish: pickerel, sunfish, bluegill, blackspotted top minnows, redfin shiners
LA01	Bayou de Loutr-	Aug. 10, 1979	0800	2.0	large mouth bass (3)
LA02	Bayou de Loutre	Aug. 10, 1979	1015	2.2	gar (2)
LA03	Corney Lake	Aug. 10, 1979	1200	2.3	gar (3)

[a] Not listed on Field Data Sheet

Table 2. SUMMARY OF ORGANIC SAMPLE EXTRACTION AND CLEANUP

Sample Code	Type of Sample	Wt. of Sample Extracted (g)	% Fat
AR2 E021	Fish	102.37	2.2
AR2 D008	Turtle Liver	103.49	2.2
AR2 D010	Turtle Organs	101.04	29.9
AR2 E018	Fish	97.06	5.1
AR2 E016	Fish	116.09	3.4
LA 01	Fish	98.56	4.6
LA 02	Fish	92.10	6.1
LA 03	Fish	119.80	1.5

tion procedure. The extracts were combined, filtered through fluted filter paper, and dried using cleaned sodium sulfate. The volumes of the extracts were adjusted to 200 mL, and a 5.0 mL portion of each sample was placed in a weighed Reactivial® and blown down under nitrogen to determine the percent fat (or percent extractables) gravimetrically. The blown-down samples were redissolved in hexane and recombined with the appropriate extracts.

All samples were partitioned into acetonitrile, and the halogenated hydrocarbons were back-partitioned into hexane, according to the procedure in the analytical protocol (Appendix C). All of the samples were processed through the Florisil cleanup procedure. The 6% ether/hexane and the 15% ether/hexane fractions resulting from the Florisil cleanup were combined, and the volumes were reduced to 1.0 mL. Due to the very high background in the GC/MS analysis (discussed below), all of the samples were chromatographed on Florisil repeatedly until no yellow coloration was observed in the concentrated extract. For the Arkansas samples (AR2xxxx) this required a total of three cleanup cycles on the Florisil chromatography column.

ANALYSIS

The samples were analyzed by gas chromatography/mass spectrometry (GC/MS). Initial attempts at analysis were impeded by interference from high levels of lipids and other background. Even after a total of three cleanup cycles on the Florisil chromatographic column, the electron impact GC/MS (GC/EIMS) spectra and selected ion plots indicated potential non-halogenated interferences even at $m/z > 800$. To confirm the GC/EIMS data, samples were submitted to GC/negative ion chemical ionization mass spectrometry (GC/NICIMS). This technique detects only the negative ions (vs. the positive ions detected in "normal" electron impact MS) and can take advantage of the electron capturing properties (like GC/ECD) of certain chemical classes. Thus, it is highly selective for halogenated organ. The full scan GC/EIMS analyses of the Arkansas samples found no brominated compounds. A typical spectrum is presented in Figure 1. The Arkansas samples (AR2xxxx) were also analyzed by GC/EIMS in the selected ion monitoring (SIM) mode which is more selective and sensitive than the full scan mode. Table 3 lists the SIM GC/EIMS conditions for several brominated compounds. A typical listing of the peak intensities is shown in Table 4. Representative single ion plots are shown in Figure 2. It is clear

that there is very high background from non-brominated compounds, giving peaks with proper retention times and apparently correct ion intensity ratios for many brominated compounds.

To confirm the presence of the brominated compounds, the samples were submitted to GC/NICIMS. Typical ion plots are shown in Figures 3-5. This technique is far more sensitive than SIM GC/EIMS, so any brominated compounds should be easily observed by the proper ratio of the m/z 79 and 81 ion plots (100/98.7). It should be noted that GC/NICIMS is a new analytical technique and is subject to the following caveats: 1) relative sensitivities of different compounds are not known; 2) all operational parameters have not been optimized; and 3) the effects of sample matrix have not been thoroughly investigated. Thus, GC/NICIMS data must be interpreted conservatively at this point. The tentative findings from SIM GC/EIMS and GC/NICIMS were then correlated. Identification of compounds required that the SIM GC/EIMS peak be confirmed by GC/NICIMS. Some peaks observed by GC/NICIMS and not by SIM GC/EIMS were labeled as "tentative" identifications due to the greater sensitivity of the former technique. The findings are presented in Table 5. It should be noted that TRIS, Tetrabrom, $C_{12}H_4Br_6$, $C_{12}H_3Br_7$, $C_{12}H_4Br_6O$, $C_{12}H_3Br_7O$, and C_6Br_5OH were tentatively identified by SIM GC/EIMS but not confirmed by GC/NICIMS. Thus, analysis by GC/EIMS alone would have yielded several false positive identifications.

No effort was made at quantitation. The high background "noise" levels in the GC/EIMS data preclude any accurate or even "rough" calculation of the response values such as those listed in Table 4. The background interference in GC/NICIMS is insignificant and quantitation should be feasible. However, the technique has not yet been validated for quantitation. Based upon the relative response of the standards and samples, it is safe to extrapolate that the brominated compounds found were at levels much less than 1 ppm.

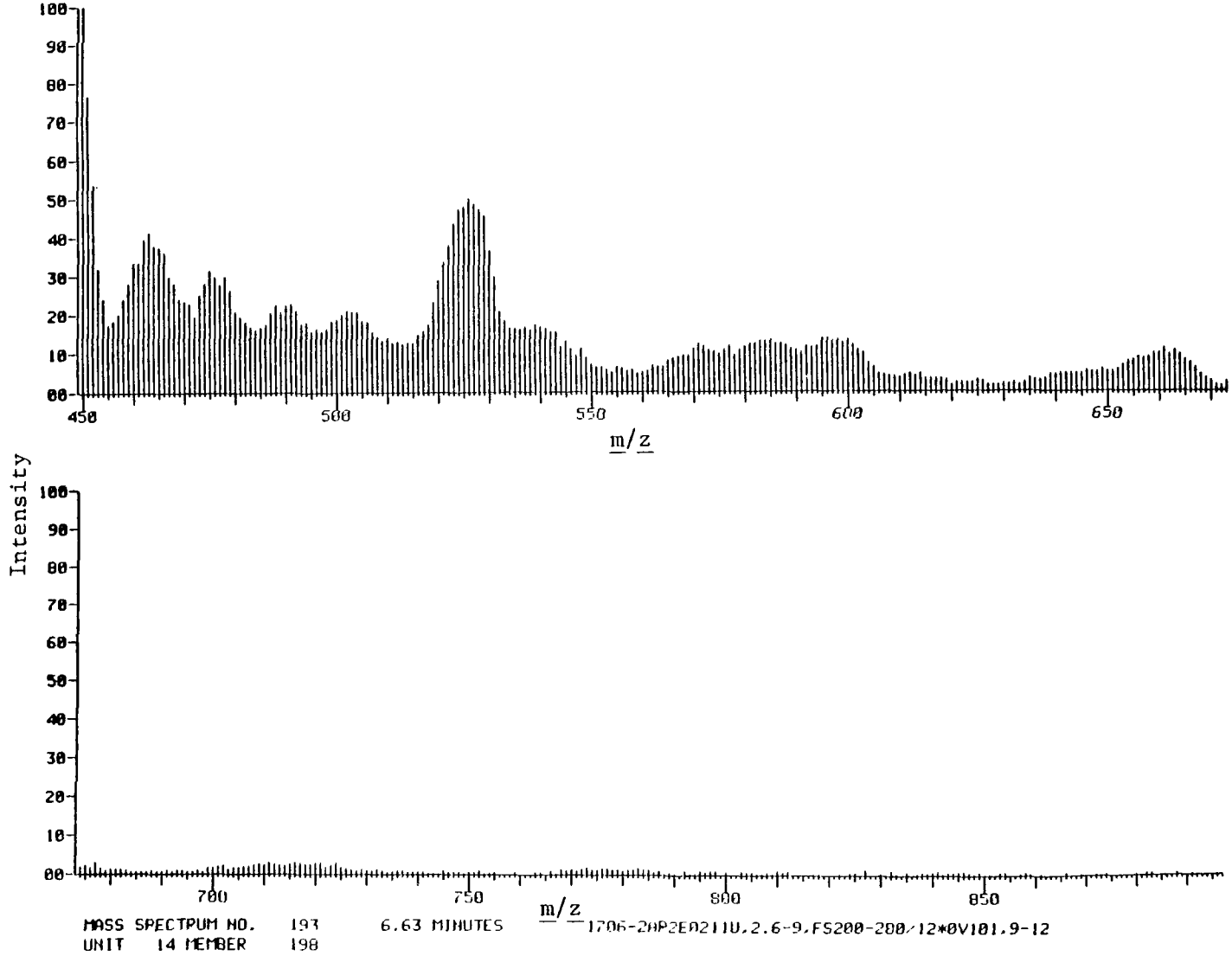

Figure 1. Full scan GC/EIMS spectrum of AR2E021 illustrating very high background.

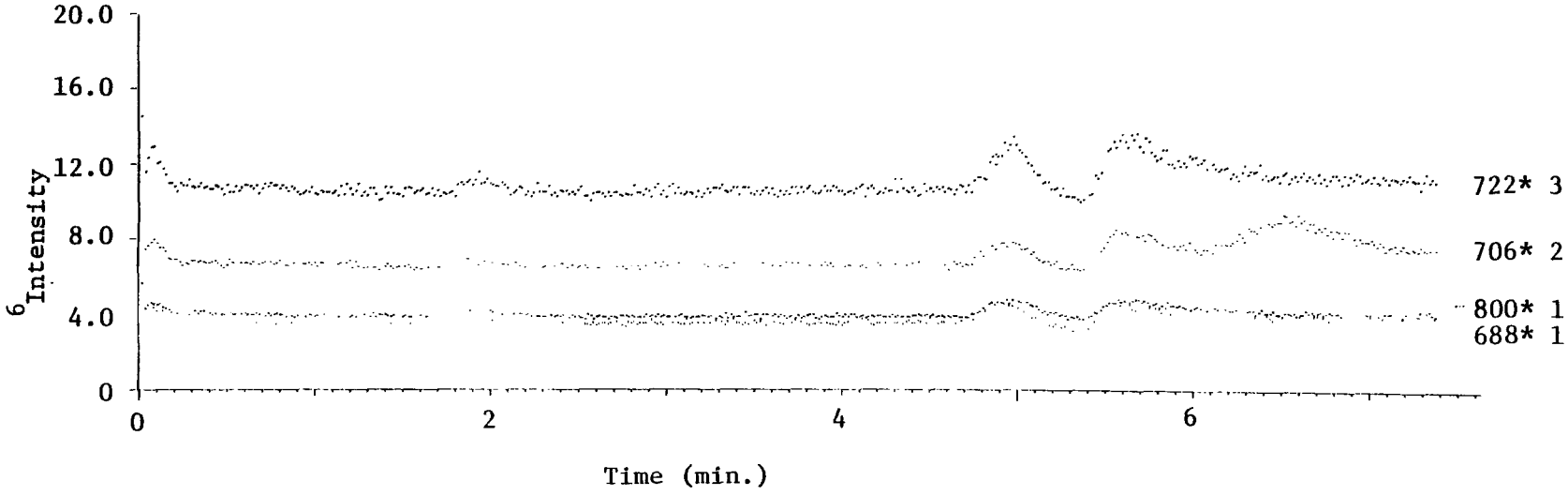

Figure 2. Single ion plots from SIM GC/EIMS analysis of AR2E021 (see Table 4 for ion intensity listings). Conditions were 45 x 0.2 cm glass column packed with 2% OV-101; column temperature was programmed from 200 - 280° at 12°/min.; carrier was helium at 30 mL/min.

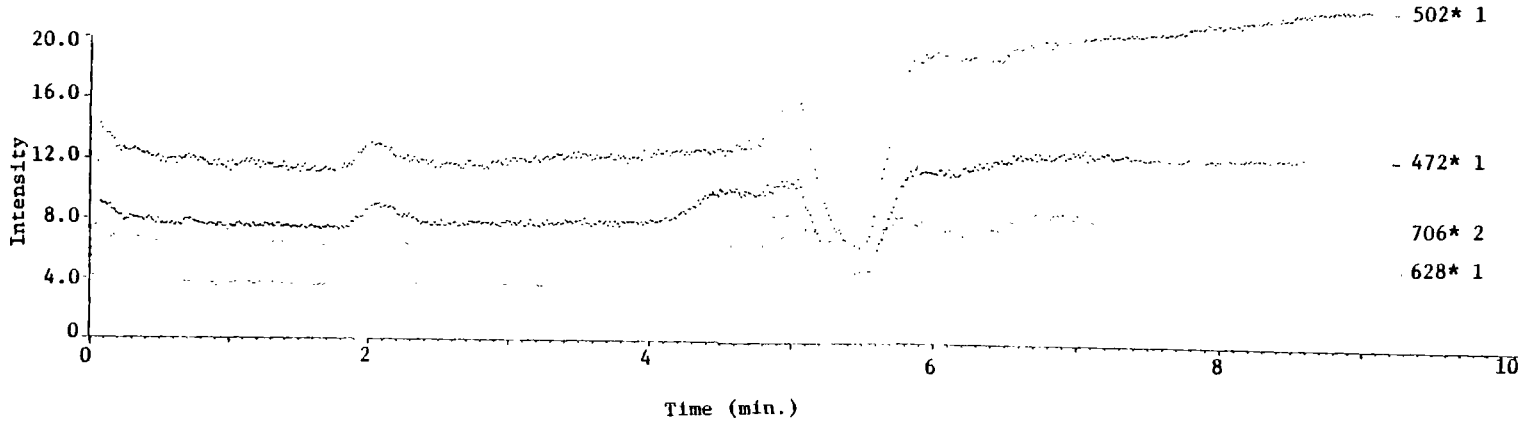

Figure 2. (continued)

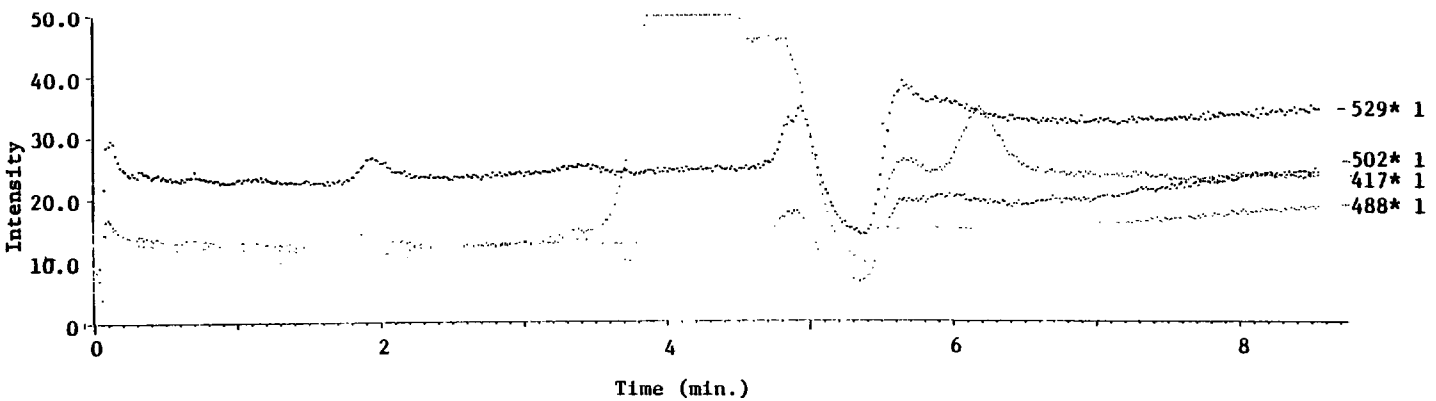

Figure 2. (continued)

Table 3. SIM MASS SPECTROMETRY CONDITIONS FOR SELECTED BROMINATED COMPOUNDS

Compound	M[a]	SIM Ions[b]	Intensity Ratio[c]
$C_{12}H_6Br_4$	466	470,472	100/65
$C_{12}H_5Br_5$	544	548,550	100/98
$C_{12}H_4Br_6$	622	628,630	100/73
$C_{12}H_3Br_7$	700	706,708	100/98
$C_{12}H_2Br_8$	778	784,788	100/96
$C_{12}HBr_9$	856	866	
$C_{12}Br_{10}$	934	942	
$C_{12}H_6Br_4O$	482	486,488,490	100/65/16
$C_{12}H_5Br_5O$	560	564,566	100/98
$C_{12}H_4Br_6O$	638	644,646	100/73
$C_{12}H_3Br_7O$	716	722,724	100/98
$C_{12}H_2Br_8O$	794	800,804	100/96
$C_{12}HBr_9O$	872	882	
$C_{12}Br_{10}O$	950	958	
Tris[d]	692	417,419	90/100
Firemaster 680[e]	682	688,690	100/73
Tetrabrom[f]	540	529,531	100/25
Pentabromophenol	484	488,490	100/98
$C_{10}Cl_{10}$ (std)	494	502	

[a] Molecular weight, based on ^{79}Br.

[b] Selected ion monitoring ions; generally most intense ions in parent or base clusters.

[c] Ratio of SIM ion intensities calculated from natural isotopic abundance ratios. Acceptable experimental ratios were ±50% of stated ratio.

[d] Tris(2,3-dibromopropyl)phosphate

[e] 1,2-Bis(2,4,6-tribromophenoxy)ethane

[f] 2,2-Bis(dibromo-4-hydroxyphenyl)propane

Table 4. RAW DATA FROM SIM GC/EIMS ANALYSIS OF AR2E021

Mass	Peak Intensity	Retention Time (min.)	Peak Area	Number of Data Points	Background Intensity	Comment
417	00.96	2.083	09.56	23	12.90	
419	01.16	1.949	12.12	23	30.22	
470	01.82	2.066	30.88	39	10.36	
472	01.48	2.066	29.02	39	07.42	
488	01.84	2.099	29.88	33	11.04	Possibly C_6Br_5OH
490	03.58	2.066	53.46	33	22.22	
502	01.92	2.000	28.28	33	14.58	
529	03.32	2.016	54.10	33	26.10	Too early for Firemaster 680
531	03.44	2.000	44.34	33	22.08	
688	00.44	2.000	03.66	26	03.78	
690	00.36	2.049	03.42	26	03.78	
529	01.62	3.416	23.80	29	26.42	Possibly Tetrabrom
531	01.14	3.449	14.90	29	22.12	
417	66.50	4.083	2188.26	65	33.54	Ions do not maximize at same time
419	35.10	4.233	1042.16	65	45.92	
688	00.56	4.299	04.14	15	03.74	No real peak
690	00.02	4.199	00.02	15	03.78	
630	02.86	4.499	66.94	43	05.84	Possibly $C_{12}H_4Br_6$
628	03.90	4.433	90.00	43	05.94	
472	01.06	4.499	19.68	38	08.94	
470	03.54	4.516	72.34	38	14.24	
419	15.16	4.932	293.22	39	31.74	Probably non-brominated background
417	12.52	4.932	222.04	35	38.00	
488	04.90	5.033	77.40	35	08.96	
490	11.22	5.033	170.24	35	16.84	
502	07.20	5.016	108.64	35	11.66	
529	12.90	5.033	193.74	35	20.70	
531	11.34	5.033	166.24	35	17.00	
688	01.16	5.066	16.76	35	03.54	
690	00.94	5.033	11.66	34	03.66	
470	03.60	5.049	44.34	27	11.44	
472	02.86	5.049	32.88	27	07.84	
502	04.78	5.049	53.98	22	11.62	
628	01.82	5.066	19.50	25	06.34	Possibly $C_{12}H_4Br_6$
630	01.54	5.066	18.78	25	05.86	
706	00.62	5.116	09.02	31	03.16	
708	00.40	5.049	05.18	31	03.00	
722	00.72	5.116	08.54	28	03.38	
724	00.90	5.099	09.56	28	03.54	
724	00.58	5.682	07.70	25	03.64	
722	00.58	5.766	07.30	25	03.64	
690	00.78	5.666	08.50	24	03.78	Most likely non-brominated background peak
688	00.66	5.716	07.26	22	04.00	
531	10.50	5.749	158.14	30	19.40	
529	13.30	5.749	196.80	29	23.62	
502	05.84	5.766	88.38	29	14.78	
490	09.52	5.766	146.56	29	20.18	
488	04.74	5.766	70.12	29	11.10	
419	11.88	5.782	193.56	29	25.56	
417	08.70	5.732	138.76	29	17.50	
630	01.98	5.732	36.38	36	04.14	
628	02.02	5.749	36.16	36	04.30	
708	00.52	5.749	08.38	33	03.22	
706	00.62	5.732	08.08	33	03.48	
502	05.28	5.799	95.26	35	12.52	
470	03.82	5.849	68.22	35	10.24	
472	03.02	5.832	50.54	35	08.32	
417	10.36	6.266	180.40	37	27.28	
419	05.30	6.199	94.30	37	38.80	
628	01.06	6.682	25.04	51	05.10	
630	00.66	6.799	15.62	51	04.90	
706	00.62	6.749	17.40	53	03.70	
708	00.62	6.849	16.84	53	03.48	

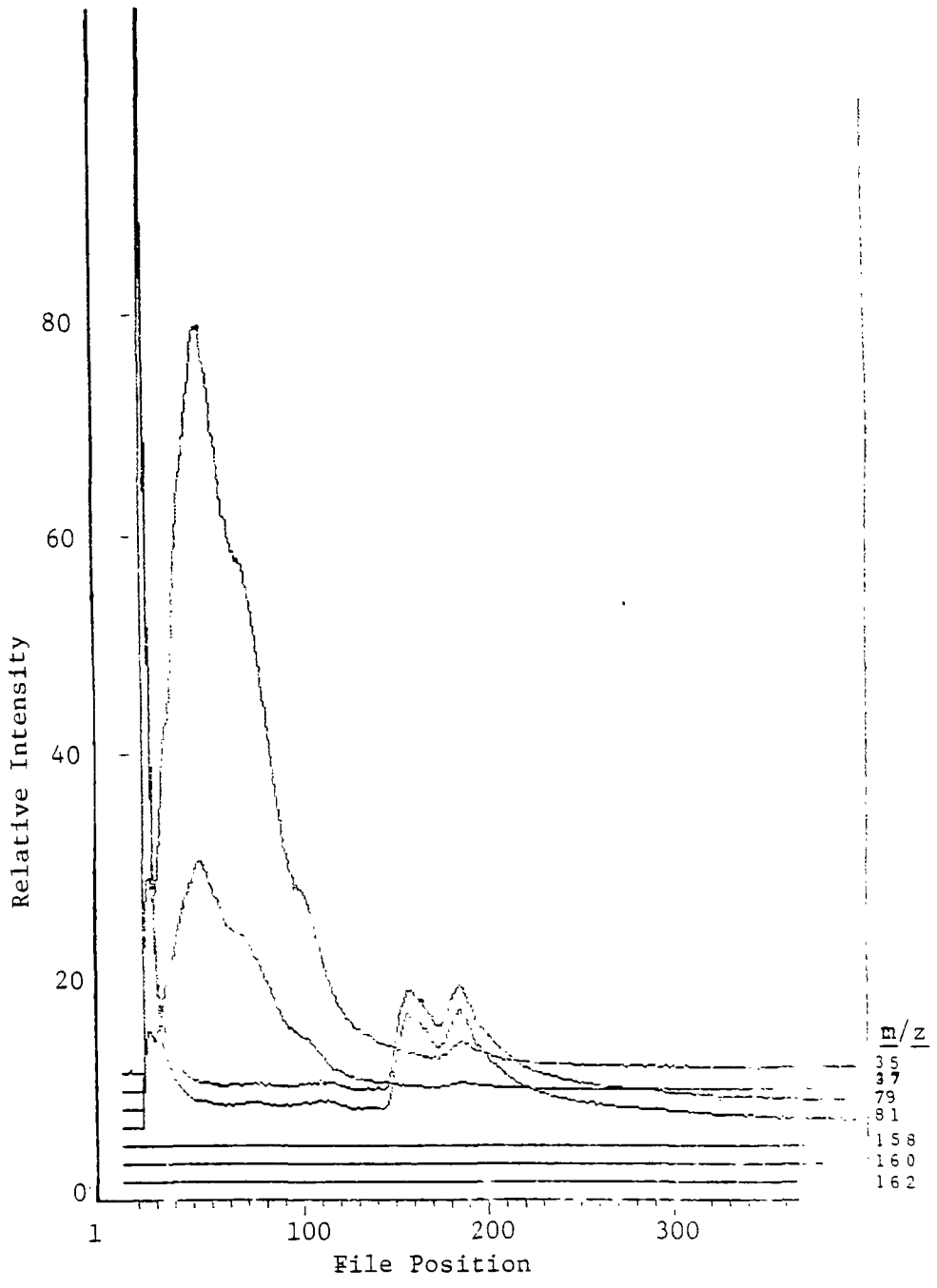

Figure 3. Single ion plots from GC/NICIMS analysis of AR2E021. Conditions were 46 x 0.2 cm 2% OV101 column with a helium flow of 13 mL/min. Column temperature was at 200° for 2 min. then programmed to 280° at 12°/min. Separator temperature was 275°, multiplier voltage 2330, trap current 500A, electron energy 50V, and ion source temperature 250°. Brominated compound at file position 158 is 10 ng $C_{12}Br_{10}$ added during previous analyses as a standard. Brominated compound at file position 182 was tentatively identified as $C_{12}Br_{10}O$.

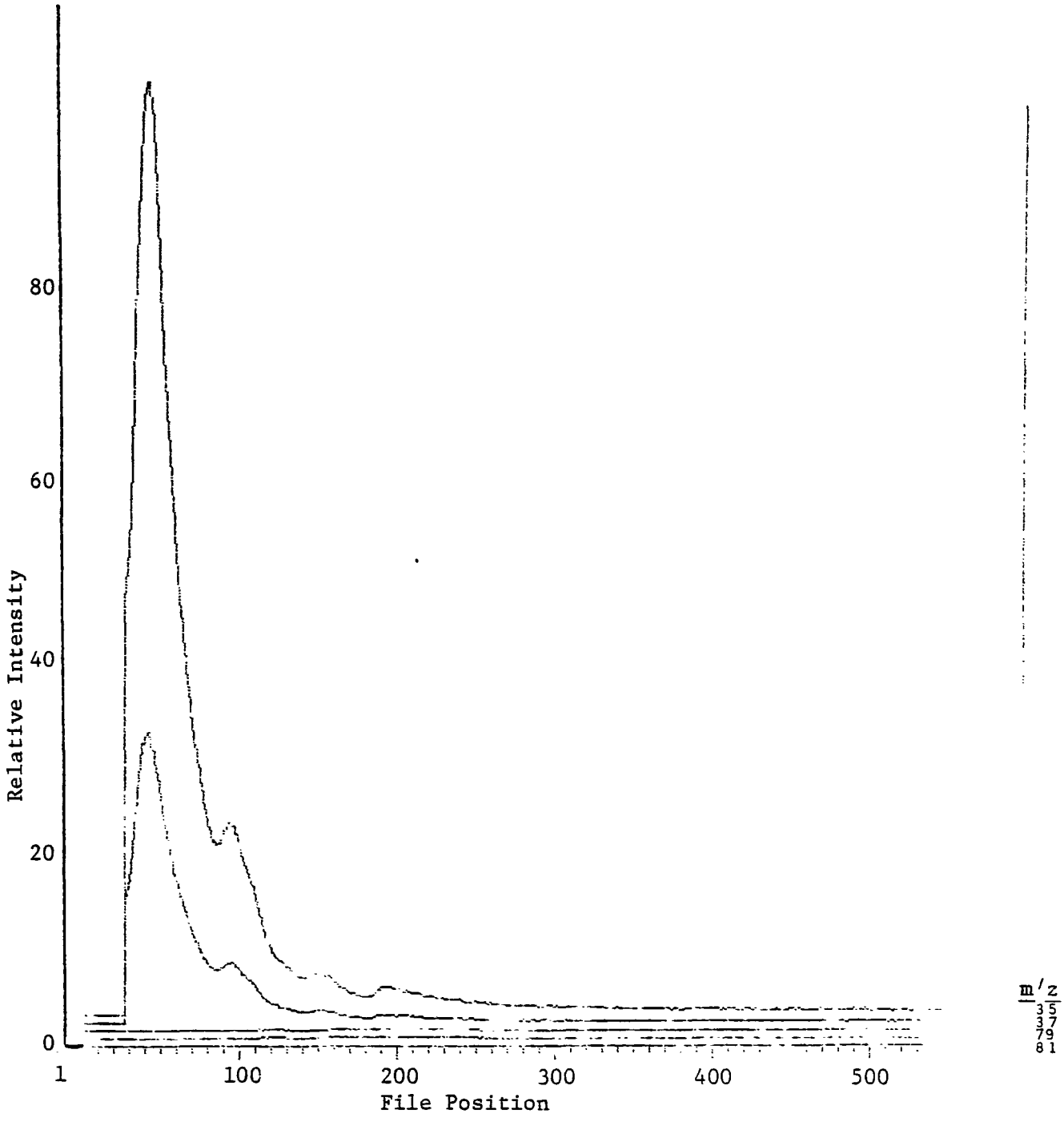

Figure 4. Single ion plots from GC/NICIMS analysis of LA01. Conditions were as in Figure 3, except the flow rate was 18 mL/min, the final column temperature was 290°C and the ion source temperature was 275°C. Note: no trace of brominated organics was observed.

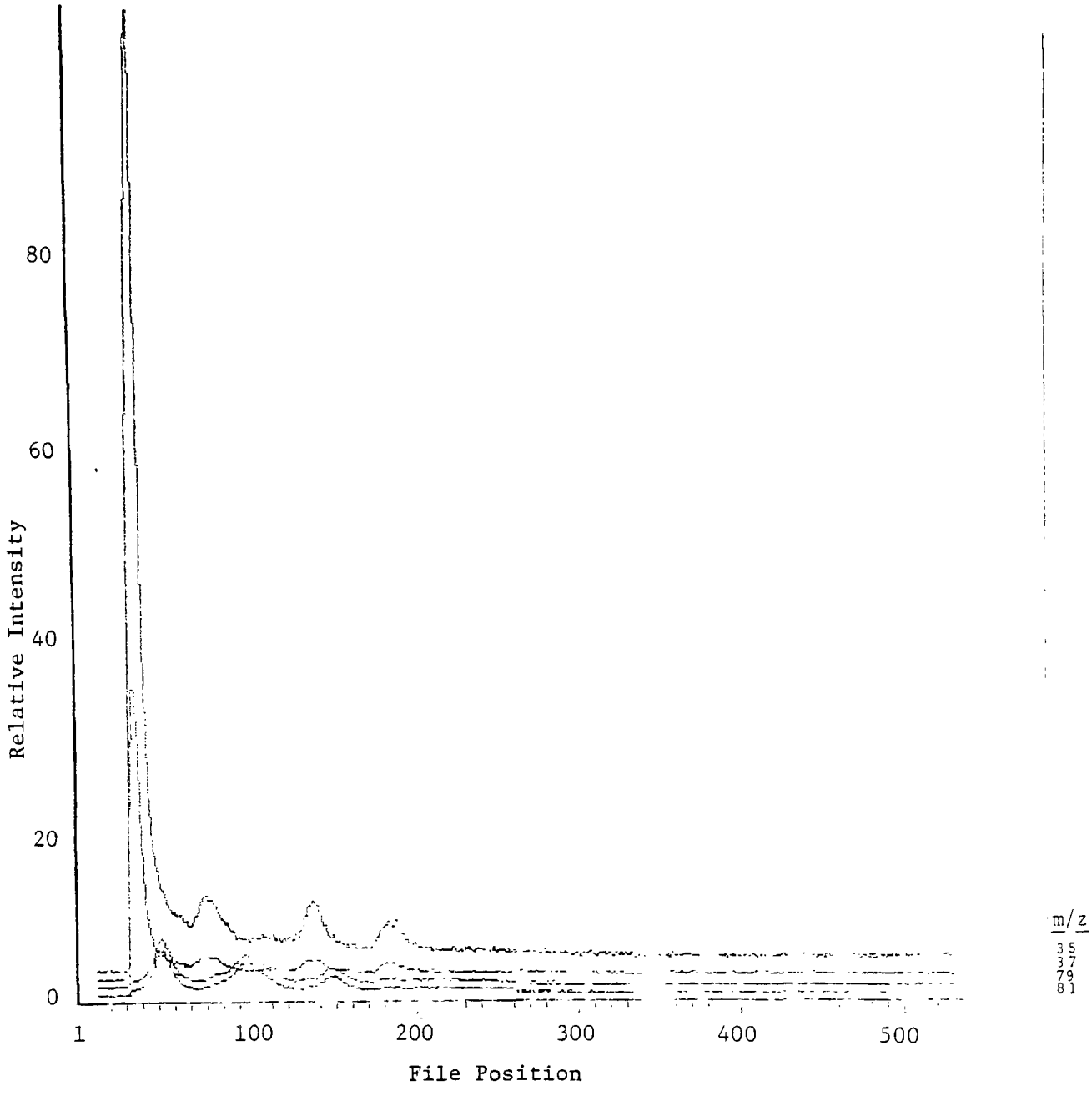

Figure 5. Single ion plots from GC/NICIMS analysis of LA03. Conditions were as in Figure 4. Three brominated organic peaks are clearly observed.

Table 5. BROMINATED COMPOUNDS FOUND IN FISH AND TURTLE SAMPLES FROM ARKANSAS AND LOUISIANA

Sample Code	Compounds Found
AR2D008	--------
AR2D010	$C_{12}H_4Br_6$ $C_{12}H_3Br_7$ $C_{12}Br_{10}O$ (tent.)[a]
AR2E016	$C_{12}Br_{10}O$ (tent.)[a]
AR2E018	$C_{12}Br_{10}O$ (tent.)[a]
AR2E021	$C_{12}Br_{10}O$ (tent.)[a]
LA01	--------
LA02	$C_{12}Br_{10}$
LA03	Three brominated compounds eluting in the range of a pentabromo-heptabromo compounds (e.g., Firemaster 680, $C_{12}H_4Br_6$, etc.)[a]

[a] GC/NICIMS data only

REFERENCES

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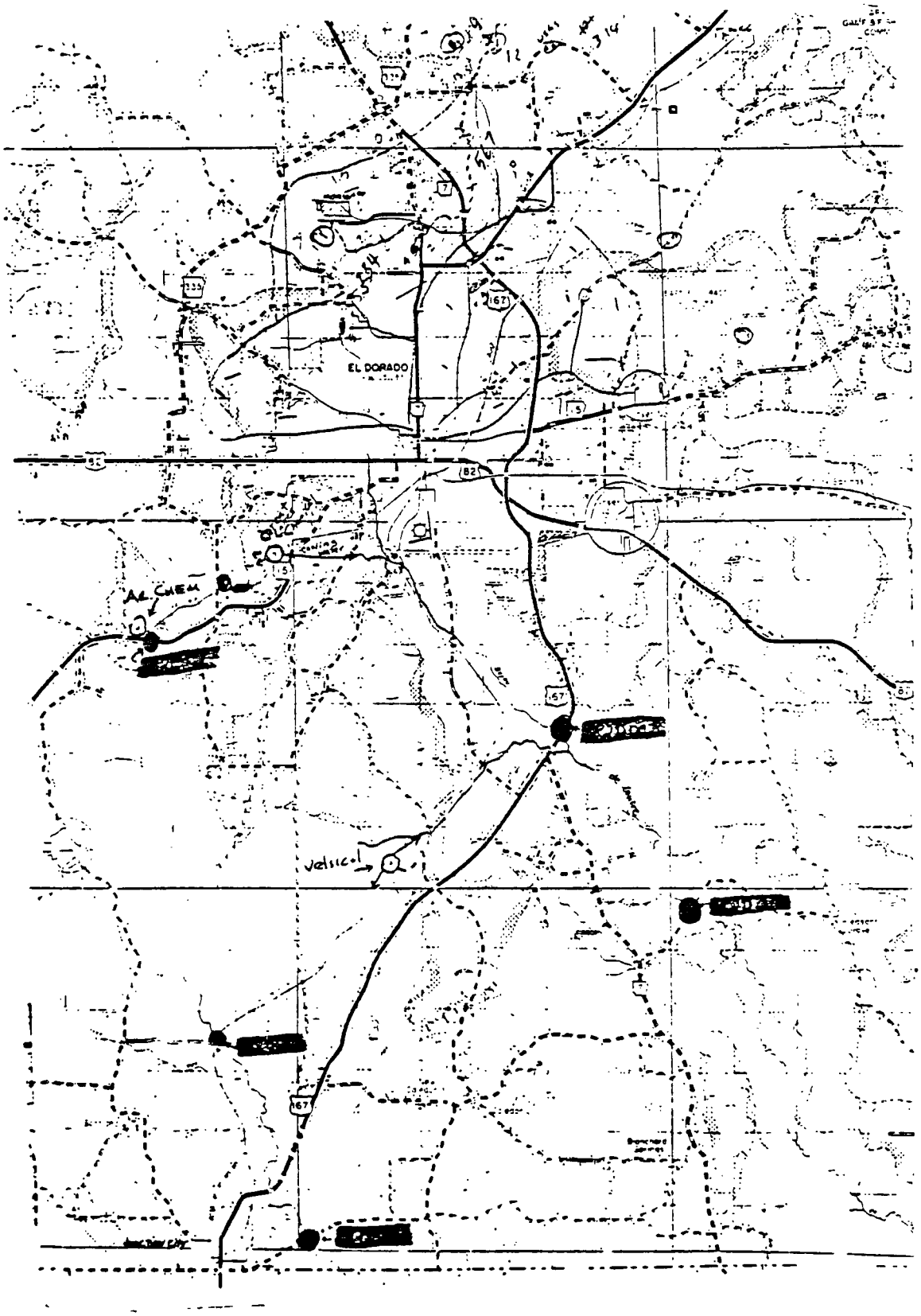
2. Zweidinger, R. A. and E. D. Pellizzari, Development of Sampling and Analysis Methodology for Tris(2,3-dibromopropyl)phosphate, Final Report on EPA Contract No. 68-01-1978, Task III, May 1978.
3. Zweidinger, R. A., S. D. Cooper, M. D. Erickson, L. C. Michael, and E. D. Pellizzari, Sampling and Analysis for Semi-Volatile Brominated Organics in Ambient Air, in Monitoring Toxic Substances, D. Schuetzle, ed., ACS Symposium Series 94, 1979, p. 217-231.

APPENDIX A

SAMPLE LOCATION MAP AND FIELD DATA SHEETS FROM ARKANSAS SAMPLING


EL DORADO
82
67
5
AL CHEM
Vetsic

Brominated Compounds Study-Fish Tissue Analysis
Field Data Sheet

Station #AR2D008

Secondary #(s) State ARK USGS _____ Other ___

Location Description - Bayou de La Utre 3.5 below El Dorado STP #1 and 3 miles below STP #2

T18S ; R14W ; S23

Station Located on Map? (Yes) No

Field Investigators Bob Singleton and John Giese

Date 7-11-79 Time 10:30 AM.

Sample # AR2D008 only (1) sample A

~~Fish Weight~~ only caught turtles at this location

~~No. of Fish~~ so will use fatty tissue and liver.

~~Length~~ _____

Species Common Name(s) (1) Common snapping turtle

Scientific Name(s) _____

Habitat aquatic

Tropic Level probably top of food chain

Sample # none B

Fish Weight _____

No. of Fish _____

Length _____

Species Common Name(s) _____

Scientific Name(s) _____

Habitat _____

Tropic Level _____

Field Measurements - Historical Data - not actually measured during fish collection.

Parameter	Value	Units	Comments
Dissolved Oxygen	1.94	mg/l	below STP *
Temperature	27°C	C	
PH	7.41		
Conductivity	3439	uMHOS	
Flow	19	cfs	
Turbidity	<25	JCU	
T. Bromine	35.67	mg/l	

Field Observations

Fish _____

Odor _____

Color _____

Turbidity _____

Vegetation _____

Scum _____

Flow _____

Other _____

Comments

Dischargers _____

Other_____

_____

Brominated Compounds Study-Fish Tissue Analysis
Field Data Sheet

Station # AR2D010

Secondary #(s) State ARK USGS _____ Other ___

Location Description - Bayou de Loutre at state Monitoring station Ouc 5.
T18S; R14W; S6

Station Located on Map? (Yes) No

Field Investigators Bob Singleton and John Giese

Date 7-11-79 Time 9:00 AM

Sample # AR2D010 only (1) sample A

~~Fish Weight~~ only caught turtles at this location so
~~No. of Fish~~ will use fatty tissue and livers for
~~Length~~ sample

Species Common Name(s) (2) alligator snappers (1) red ear slider

Scientific Name(s) _____

Habitat aquatic

Tropic Level probably top of food chain

Sample # _____ B

Fish Weight _____

No. of Fish _____

Length _____

Species Common Name(s) _____

Scientific Name(s) _____

Habitat _____

Tropic Level _____

Field Measurements

Parameter	Value	Units	Comments
Dissolved Oxygen	6.07	mg/l	*
Temperature	19.4°	C°	yearly
PH	7.0		
Conductivity	2853.81	yMHO's	
Flow	96	CFS	
Turbidity	20	JTU's	

Field Observations

Fish _____

Odor _____

Color _____

Turbidity _____

Vegetation _____

Scum _____

Flow _____

Other _____

_____

_____

Comments

Dischargers All industrial area of El Dorado drains in to de Loutre above this point

_____

_____

Other_____

_____

Brominated Compounds Study-Fish Tissue Analysis
Field Data Sheet

Station # AR2E016

Secondary #(s) State ARK USGS _____ Other ___

Location Description - Cornie Bayou 1.5 miles below Junction City STP.

T20S; R15W; S6

Station Located on Map? (Yes) No

Field Investigators Bob Singleton and John Giese

Date 7-10-79 Time 10:00 AM

Sample # AR2E016 A

Fish Weight _____

No. of Fish list on back page

Length _____

Species Common Name(s) _____

Scientific Name(s) _____

Habitat _____

Tropic Level _____

Sample # None B

Fish Weight _____

No. of Fish _____

Length _____

Species Common Name(s) _____

Scientific Name(s) _____

Habitat _____

Tropic Level _____

Field Measurements - Historical Data - not actually measured at time of fish collection.

Parameter	Value	Units	Comments
Dissolved Oxygen	6.7	mg/l	*
Temperature	17°	C	~~Yearly avg.~~
PH	7.1		
Conductivity	572	µMHOS	
Flow	106	cfs	
Turbidity	23	JCU's	

Field Observations

Fish _____

Odor _____

Color _____

Turbidity _____

Vegetation _____

Scum _____

Flow _____

Other _____

_____

_____

Comments

Dischargers _____

_____

_____

_____

* Other_____

_____

AR2E016

	estimate weight/lbs	length/inches
1 yellow bullhead	.7	12"
1 black bullhead	.5	11"
1 bluegill sunfish	.1	4"
1 bluegill sunfish	.3	6"
1 spotted sucker	.5	14"

due to size of total catch should composite all fish for one sample.

J. Giese

Brominated Compounds Study-Fish Tissue Analysis
Field Data Sheet

Station # AR2E018

Secondary #(s) State_____ USGS_____ Other___

Location Description - Cornie Bayou 6 miles below Arkansas Chemical

T18S; R15W; S2

Station Located on Map? (Yes) No

Field Investigators Bob Singleton and John Giese

Date 7-11-79 Time 11:30 AM

Sample # AR2E018 A

Fish Weight _____

No. of Fish list on back page

Length _____

Species Common Name(s) _____

Scientific Name(s) _____

Habitat _____

Tropic Level _____

Sample # _____ B

Fish Weight _____

No. of Fish _____

Length _____

Species Common Name(s) _____

Scientific Name(s) _____

Habitat _____

Tropic Level _____

Field Measurements - Historical Data - not actually measured during fish collection.

Parameter	Value	Units	Comments
Dissolved Oxygen	5.43	mg/l	*
Temperature	26°	C	
PH	6.40		
Conductivity	468	u MHOS	
Flow	.30	cfs	
Turbidity	<25	JCU's	
T. Bromine	11.7	mg/l	

Field Observations

Fish _____

Odor _____

Color _____

Turbidity _____

Vegetation _____

Scum _____

Flow _____

Other _____

_____

_____

Comments

Dischargers _____

_____

_____

_____

Other_____

_____

AR2E018

		weight/lbs	estimate length/inches
1	Largemouth Black Bass	.5	10"
6	longear sunfish	.3	5" (avg)
20	bluegill sunfish	.3	5" (avg)
1	crappie	.1	5"
2	warmouth Bass	.1	5"

Brominated Compounds Study-Fish Tissue Analysis
Field Data Sheet

Station # AR2E021

Secondary #(s) State ARK USGS _____ Other ___

Location Description - Tributary of Cornie Bayou immediately east of Arkansas Chemical on Highway 15. T18S; R16W; S10

Station Located on Map? (Yes) No

Field Investigators _____

Date 7-10-79 Time 2:00 PM

Sample # AR2E021 A

Fish Weight _____

No. of Fish list on back page

Length _____

Species Common Name(s) _____

Scientific Name(s) _____

Habitat _____

Tropic Level _____

Sample # _____ B

Fish Weight _____

No. of Fish _____

Length _____

Species Common Name(s) _____

Scientific Name(s) _____

Habitat _____

Tropic Level _____

Field Measurements - no data available

Parameter	Value	Units	Comments
Dissolved Oxygen			*
Temperature			
PH			
Conductivity			
Flow			
Turbidity			

Field Observations

Fish _____

Odor _____

Color _____

Turbidity _____

Vegetation _____

Scum _____

Flow _____

Other _____

_____

_____

Comments

Dischargers _____

_____

_____

_____

Other_____

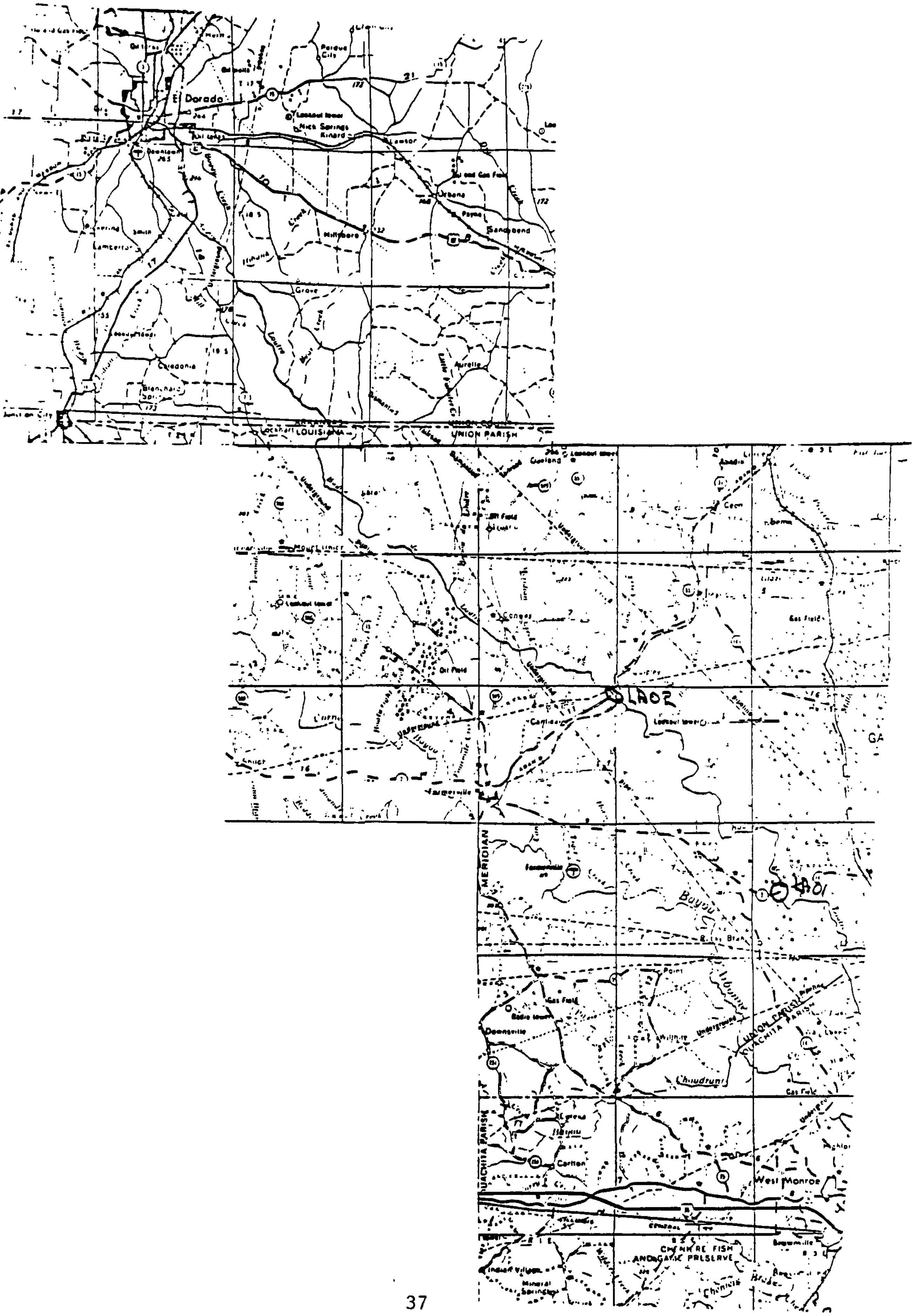
_____

This stream was very small. Had to actually use minnow seine. All fish were very small. Should probably make one composik sample from all.

3	Grass pickerel
1	longear Sunfish
13	small bluegill
5	Blackspotted Top minnows
7	redfin Shiners

APPENDIX B

SAMPLE LOCATION MAP AND FIELD DATA SHEETS FROM LOUISIANA SAMPLING


El Dorado
Nick Springs
Lawson
Urbana
Sandybend
Hillsboro
Grove
Caledonia
Lambert
Aurelle
Junction City
ARKANSAS
LOUISIANA
UNION PARISH
Lockhart
Oil Field
Farmerville
LA02
LA01
Bayou
Lookout tower
Gas Field
Downsville
Radio tower
UNION PARISH
OUACHITA PARISH
MERIDIAN
OUACHITA PARISH
Calhoun
West Monroe
CHENIERE FISH AND GAME PRESERVE
Indian Village
Mineral Springs

Brominated Compounds Study-Fish Tissue Analysis
Field Data Sheet

Station # LA01

Secondary #(s) State_____ USGS_____ Other___

Location Description - Bayou De Lutre at Hwy 2 Bridge

La Station # S08-0210-010

Union Parish, La.

Station Located on Map? Yes/No

Field Investigators Louis R. C. Johnson

Date 10 August Time 08:00

Sample # _____ A

Fish Weight 2 lbs

No. of Fish 3

Length 2 (9 inches) 1(10 inches)

Species Common Name(s) LM Bass

Scientific Name(s) ~~Micropterus Salmoides~~

Habitat _____

Tropic Level Preditor

Sample # 2 B

Fish Weight 1.5 lb

No. of Fish 5

Length 3 inches to 6 inches

Species Common Name(s) Bream

Scientific Name(s) Lepomis species

Habitat _____

Tropic Level Non Preditory food fish

Field Measurements

Parameter	Value	Units	Comments
Dissolved Oxygen			
Temperature			
PH			
Conductivity	NONE		
Flow			
Turbidity			

Field Observations

Fish yes

Odor None

Color Dark

Turbidity

Vegetation Yes

Scum None

Flow Average

Other

Comments

Dischargers

Other_____

_____

Brominated Compounds Study-Fish Tissue Analysis
Field Data Sheet

Station # LA02

Secondary #(s) State _____ USGS _____ Other ___

Location Description - Bayou DeLutre Huey 33

Bridge Union Parish Louisiana

Station Located on Map? Yes/No

Field Investigators L. R. C. Johnson

Date 10 August Time 10:15 hrs

Sample # _____ A

Fish Weight 2 lbs, 3 oz.

No. of Fish 2

Length 15 inches

Species Common Name(s) Gar

Scientific Name(s) Lepisoteus species

Habitat Preditor

Tropic Level _____

Sample # _____ B

Fish Weight _____

No. of Fish _____

Length _____

Species Common Name(s) _____

Scientific Name(s) _____

Habitat _____

Tropic Level _____

Field Measurements

Parameter	Value		Units	Comments
Dissolved Oxygen				
Temperature				
PH		NONE		
Conductivity				
Flow				
Turbidity				

Field Observations

Fish Some seen

Odor None

Color Amber

Turbidity No

Vegetation None

Scum None

Flow Moderate

Other

Comments

Dischargers

Other_____

_____

Brominated Compounds Study-Fish Tissue Analysis
Field Data Sheet

Station # LA03

Secondary #(s) State_____ USGS_____ Other___

Location Description - ~~Corney Lake along south bank east of US~~ Forestry service Boat Launch Claiborne Parish, Louisiana

Station Located on Map? Yes/No

Field Investigators L. R. C. Johnson

Date 10 August Time 12:00 hrs

Sample # _____ A

Fish Weight 2 lbs, 4 oz

No. of Fish 3

Length 15 inches

Species Common Name(s) Gar

Scientific Name(s) Lepisosteus species

Habitat _____

Tropic Level Preditor

Sample # _____ B

Fish Weight _____

No. of Fish _____

Length _____

Species Common Name(s) _____

Scientific Name(s) _____

Habitat _____

Tropic Level _____

Field Measurements

Parameter	Value	Units	Comments
Dissolved Oxygen			
Temperature			
PH			
Conductivity			
Flow	NONE		
Turbidity			

Field Observations

Fish Some

Odor None

Color Clear

Turbidity Clear

Vegetation Heavy

Scum None

Flow None

Other

Comments

Dischargers

Other_____

_____

APPENDIX C

ANALYTICAL PROTOCOL: SAMPLING AND ANALYSIS OF EXTRACTABLE HALOGENATED ORGANICS IN TISSUE

ANALYTICAL PROTOCOL: SAMPLING AND ANALYSIS OF EXTRACTABLE HALOGENATED ORGANICS IN TISSUE

1.0 Principle of Method

Semi-volatile halogenated hydrocarbons are extracted from tissue samples with organic solvents, dried, and concentrated to an appropriate volume for quantification using GC/ECD. Identifications are confirmed by GC/ECD using a second column and, when sufficiently concentrated, by GC/MS/COMP. Samples are optionally subjected to liquid chromatographic cleanup on Florisil to remove lipids if severe interferences are encountered. This procedure was adapted from that of Thompson (A1).

2.0 Range and Sensitivity

The sensitivity of response to GC/ECD is a function of the instrument, the compound, and the matrix from which it is extracted. The detection limit for GC/ECD analysis is 1-5 ng/g (ppb), depending on compound and instrumental conditions.

3.0 Interferences

Interferences in sample analysis and quantification using GC/ECD are manifested in the electron capturing ability of the given contaminant. Blood extracts which have not been cleaned up contain interferences which can largely be removed by gradient liquid-liquid chromatography on 2% aqueous deactivated Florisil and/or back partitioning with acetonitrile, as discussed below.

4.0 Precision and Accuracy

Preliminary recovery results, shown in Table A-1 indicate that recoveries are from 60-90% for several types of tissue. Further recoveries will be determined with individual samples as they are analyzed throughout the program.

5.0 Apparatus

5.1 Sampling Apparatus

Samples must be collected and stored with a minimum potential for contamination or loss of more volatile components. The primary cause of contamination is from plasticizers (e.g., phthalates) in plastic and rubber. Therefore contact with these materials must be minimized or eliminated.

Table A-1. RECOVERY OF EXTRACTABLE HALOGENATED HYDROCARBONS FROM HUMAN TISSUE EXTRACTS

Tissue	Percent Extractable Material[a]	Percent Recovery[b]
Adipose[c]	84.3	76.6
Brain	4.4	69.7
Liver	1.1	85.1
Kidney	1.1	64.5
Spleen	1.3	91.2
Lung	0.4	87.5

[a] Also described as "percent fat" in some procedures.

[b] Recovery of 198 ng aldrin added to tissues after maceration and before extraction as an internal standard. Percent recovery determined after all analytical manipulations. Aldrin represents a suitable standard, since it is metabolized to endrin and has not been found in tissues. Mean recovery for adipose tissues = 79.1 $\pm$ 10.6%.

[c] Analytical workup includes acetonitrile partitioning to reduce fat content.

Samples should be stored in glass jars with foil-lined or (preferably) teflon-lined screw caps. The bottles must be thoroughly cleaned and oven-treated prior to use.

5.2 Extraction Apparatus

Beakers (500-1000 ml), 500 ml Kuderna-Danish evaporators (or 10 ml microevaporators) and receiving tubes, three ball Snyder columns, glass bottles and caps equipped with Teflon liners, reactivials®, centrifuge, and 22 mm i.d. chromatography columns. Solvent: hexane, distilled in glass and redistilled prior to use. Reagents: sea sand, anhydrous sodium sulfate, (extracted with pentane in Soxhlet extractor for 24 hr and stored in an oven at 140°C), 60/100 mesh reagent Florisil.

6.0 Procedure

6.1 Collection of Samples

It is anticipated that tissue samples collected from cadavers or surgery will be obtained from a pathologist. Personnel from RTI will work with pathologists advising them of proper sample handling procedures. To be of use for extractable halogenated organics a tissue sample must be collected a short time following death and immediately frozen in a cleaned glass container with as small a "headspace" as possible. Any handling or storage in contact with polymeric materials represents potential contamination.

6.2 Extraction, Cleanup, and Concentration

Tissue fractions are analyzed for extractable halogenated organics using a modified procedure by Thompson (A1). Approximately five grams of each tissue is ground in a large glass beaker with acid-washed sea sand and sodium sulfate (both cleaned up prior to use by extraction in a Soxhlet extractor with hexane) using a glass rod until a dry, granular mass is obtained. Aldrin, 198 ng in 100 µl hexane, is added to the sample as an internal standard. Each tissue is then extracted, with vigorous grinding, with three 50 ml aliquots of hexane for approximately 5 min each. The extracts are then filtered, concentrated in a Kuderna-Danish (KD) apparatus to approximately 10 ml, blown down under nitrogen to dryness at room temperature and weighed to obtain a value for the percent extractable material ("percent fat").

The high lipid content of adipose tissue extract necessitates partitioning of the extract into acetonitrile and back-partitioning of the halogenated hydrocarbons into hexane. Approximately 2.5 grams of fat extract is dissolved in 12 ml hexane and extracted two min each with four 30 ml aliquots of redistilled acetonitrile. The extracts are combined with 250 ml 2% aqueous sodium chloride and back-extracted with four 30 ml aliquots of hexane. The extracts are combined, dried over Na_2SO_4, concentrated in a KD to about 5 ml, blown down under nitrogen to approximately 2 ml, and subjected to Florisil cleanup as described below.

Florisil (60/100 mesh, activated at 130°C overnight) columns (2.2 cm x 10 cm) with glass frits or glass wool plugs are packed in hexane solvent. Each tissue extract is transferred to the surface of the column in approximately 2 ml of solvent, and the column walls are washed with approximately 4 ml of hexane. The halogenated hydrocarbons are then eluted with 200 ml each of 6% ether/hexane and 15% ether/hexane respectively. Each fraction is concentrated in a KD apparatus to approximately 5 ml. The 6% eluants are blown down under ambient nitrogen to appropriate volumes and immediately analyzed by GC/ECD.

Previous studies by Thompson suggest the following halogenated hydrocarbons should be found in the 6% eluant: BHC isomers, p,p'-DDE, p,p'-DDT, heptachlor, heptachlor epoxide, mirex, PCB, hexachlorobenzene, and trifluralin (H1). These represent the same general polarity of the halogenated compounds of interest in tissue samples, so this fraction is of primary interest for analysis. Extracts are dried a minimum of 30 minutes over about 0.5 g anhydrous Na_2SO_4. The extract is transferred to a 500 ml KD flask (or micro KD), topped with a Snyder column, concentrated to ca. 2-4 ml, and cooled to ambient temperature. The sides of the KD are rinsed with about 1.5 ml hexane and the extract is then blown down under nitrogen to about 1 ml, transferred to a reactivial® previously calibrated to a specific volume, and further concentrated.

6.3 Instrumental

The detection and quantification of semi-volatile halogenated hydrocarbons is made using a Series 4400 Fisher/Victoreen Gas Chromatograph equipped with a tritium foil electron capture detector. Separation is effected on a

40 m, 0.38 mm i.d., glass SCOT capillary column coated with 1% SE-30 on 0.32% Tullanox (A2,A3). Maximum efficiency is obtained with a flow rate of 2.5 ml/min of nitrogen gas with makeup nitrogen gas adjusted to a total flow of 25.0 ml/min, column 220°C (isothermal), and detector 285°C.

As a confirmatory column a 190 cm x 0.2 cm i.d. 1.5% OV-17/1.95% QF-1 on 80/100 Chromosorb W-HP packing is employed. Efficient responses are obtained for flow rates of 18 ml/min at identical column and detector temperatures.

Final confirmation of the identity of the components of sufficiently concentracted extracts (generally greater than 10 ng/µl) can be made using GC/MS/COMP.

The GC/MS/COMP systems used are a Finnigan 3300 GC/MS/COMP and an LKB 2091 GC/MS equipped with an LKB 2031 data system. Chromatographic conditions for the Finnigan 3300 are 20 m x 0.38 mm i.d., 1% SE-30 SCOT capillary operated isothermally at 235°C and a flow rate of 2.0 ml/min helium. Splitless injection (0.2-0.3 µl) is used, with standard electron impact (70 eV) ionization conditions.

The LKB 2091 is operated using a 18 m 1% SE-30/$BaCO_3$ WCOT capillary column at 240°, isothermal for PCBs and a 40 m x 0.38 mm i.d. 1% SE-30 SCOT capillary column at 230° isothermal for the pesticides. In both cases, the column flow rate is 2 ml/min with 20 ml/min split off at the injector. The mass spectrometer is operated under standard electron impact conditions.

6.4 Qualitative and Quantitative Analysis

6.4.1 Qualitative Analysis

Alternate single injections of extracts and standard solutions is the routine procedure for processing samples. If the retention time of a given component of an extract suggests the presence of a standard compound, a repetitive injection is then made. Tentative identification is made if the deviation between the two respective means is no greater than three percent. A similar criterion is then applied to the retention times of both extract and standard component upon a second, confirmatory, column. Qualitative identification of a component is made if both criteria are satisfied.

6.4.2 Quantitative Analysis

A mean linear response range of 5-160 pg/μl has been established for the compounds trifluralin and γ-BHC on a 1% SE-30/0.32% Tullanox 40 m, 0.38 mm i.d. SCOT capillary column installed in a Series 4400 Fisher/Victoreen Gas Chromatograph. Quantification of given component is made by a comparison of the means of recorder trace areas of two extract and two standard solutions within this linear response range. The precision of the concentration of a given component is normally less than ten percent of the mean concentrations and is obtained by propagation of the standard deviations of the responses of both the extract and standard solutions. The effective concentration multiplied by the volume of extract results in the total amount of extracted material.

If the extracts are deep yellow, the presence of lipids may interfere with either analysis or concentration of the extracts due to precipitation. In this case, the sample should be transferred to a 22 mm i.d. column containing 1.6 g of 2% aqueous-deactivated Florisil and eluted with 10 ml each of hexane, 5% $MeCl_2$/hex, 10% $MeCl_2$/hex, 15% $MeCl_2$/hex, 20% $MeCl_2$/hex, 30% $MeCl_2$/hex, 50% $MeCl_2$/hex, and $MeCl_2$. The extracts are concentrated and analyzed. Most semi-volatile halogenated hydrocarbons are expected to appear in the first five fractions. This estimate is based upon elution data of pesticides on Florisil (A4) and has not been subjected to full experimental verification.

6.4.3 GC/MS/COMP Confirmation

The chromatography conditions are similar to those used for GC/ECD. The samples for this study are to be screened by GC/ECD and confirmed (if sufficiently concentrated) by GC/MS/COMP. Therefore, the retention times of the two techniques must be similar. GC/ECD must operate isothermally, so the GC/MS/COMP conditions reflect this restriction.

The Finnigan 3300 and the LKB 2091 systems may be operated in both the full scan and selective ion monitoring (SIM) modes. In the full scan mode, full spectra are collected. Spectra or mass fragmentograms (single ion plots) may be plotted for interpretation. In the SIM mode, only a small number (up to 9 for the Finnigan 3300 and up to 16 for the LKB 2091) of ions are monitored. Full spectra are not collected. The advantage of this

method is that the detector spends more time "looking" at the selected ion and therefore better (generally 10-50 times) sensitivity is obtained.

To determine the limits of detection, standard solutions of selected pesticides and PCB isomers have been analyzed on the Finnigan 3300 and LKB 2091. In the full scan mode, the limit of detection was the amount of compound required for an interpretable spectrum. In the SIM mode, the limit of detection was the amount of compound required to yield a peak 2-4 times the noise level.

The estimated limits of detection for the Finnigan 3300 and LKB 2091 are presented in Table A-2.

Quantitation using GC/MS/COMP is achieved by comparing the computer-calculated integrated area of the unknown with the integrated response for a known amount of standard. To compensate for differences in ionization cross-section, the relative molar response of authentic compounds is obtained.

The calculation of the relative molar response (RMR) factor allows the estimation of the levels of sample components without establishing a calibration curve. The RMR is calculated as the integrated peak area of a known amount of the compound, A°_{unk}, with respect to the integrated peak area of a known standard, A°_{std} (in this case d_{10}-pyrene), according to the equation

$$R = \frac{A^{\circ}_{unk}/moles_{unk}}{A^{\circ}_{std}/moles_{std}} = \frac{(A^{\circ}_{unk})\ (mw_{unk})\ (g_{std})}{(A^{\circ}_{std})\ (mw_{std})\ (g_{unk})} \qquad \text{(Eq. 1)}$$

From this calculated value, the concentration of an identified compound in a sample is calculated by rearranging Equation 1 to give

$$g_{unk} = \frac{(A_{unk})\ (mw_{unk})\ (g_{std})}{(A_{std})\ (mw_{std})\ (RMR)} \qquad \text{(Eq. 2)}$$

The use of RMR for quantitation by GC/MS has been successful in repeated applications to similar research problems.

The RMRs for the compounds were calculated from the numerical integrations of peaks observed in the appropriate SIM channel. Typical RMRs listed in Table A-3 and A-4 are mean values of three injections of each of three replicate standard mixtures.

Table A-2. ESTIMATED LIMITS OF DETECTION FOR EXTRACTABLE HALOGENATED ORGANICS ANALYSIS[a]

Compound	LKB 2091[b]			Finnigan 3300[a]		
	Full Scan	SIM		Full Scan	SIM	
	ng/µl	m/z	ng/µl	ng/µl	m/z	ng/µl
trifluralin	12	264	0.4	5-10	264	<0.5
atrazine	>12<20	200	0.4	<50	200	5-10
γ-BHC (lindane)	>12<20	181	0.10-0.4	5-10	181	1
heptachlor	12	272	0.10-0.4	10-20	272	1-1.5
chlordane	∿30[c]	375	5	25-50	375	5-10
p,p'-DDE	12	246	>0.3	5-10	246	0.5-1
2-chlorobiphenyl	∿1	188	0.004	∿2.5	188	∿0.025
hexachlorobiphenyl	<1	360	∿0.016	25-50	360	∿0.15
decachlorobiphenyl	12	498	0.42	150	498	∿0.3

[a] See text for conditions.

[b] 15:1 split at injection, only 1/15 of injection is on column.

[c] 0.2 µl injected with no split.

Table A-3. RMRs FOR PCBs AND PESTICIDES OF INTEREST TO THIS PROGRAM[a]

Compound	Concentration	Ion	RMR
2-chlorobiphenyl	104 ng/µl	188	elutes with solvent and was two scans wide - not determinable
	3.8 ng/µl		
hexachlorobiphenyl	570 ng/µl	360	.38 ± 3%
	10.4 ng/µl		.35 ± 10%
decachlorobiphenyl	1156 ng/µl	498	.14 ± 7%
	8.4 ng/µl		not determinable
trifluralin	100 ng/µl	264	1.32 ± 20%
atrazine	100 ng/µl	200	.74 ± 7%
		202	.25 ± 8%
lindane	100 ng/µl	181	.74 ± 9%
		183	.62 ± 12%
heptachlor	100 ng/µl	272	.74 ± 6%
p,p'-DDE	100 ng/µl	246	.45 ± 6%
chlordane (peak 1)	100 ng/µl	373	.71 ± 5%
		375	.65 ± 5%
chlordane (peak 2)	100 ng/µl	373	.051 ± 6%
		375	.045 ± 13%

[a]Standard is d_{10}-pyrene (m/z = 212).

Table A-4. RMR FACTORS FOR STANDARD PCB SOLUTIONS, SELECTED ION MONITORING MODE

	Standard	RMR m/z 188 2-Chlorobiphenyl	RMR m/z 358 Hexachlorobiphenyl	RMR m/z 498 Decachlorobiphenyl
I	PCB-STD-20	0.60	0.257	0.341
II	PCB-STD-2	0.620 0.811 0.466 0.643 } 0.640 ± .171	0.291 0.334 0.319 0.321 } 0.325 ± .009	0.430 0.474 0.462 0.431 } 0.456 ± .018
III	PCB-STD-0.2	0.566 0.840 0.637 0.597 0.705 } 0.699 +.171	0.366 0.293 0.301 0.239 0.273 } 0.294 ± .072	0.372 0.361 0.373 0.303 0.394 } 0.361 ± .033
IV	PCB-STD-0.04	1.020 0.692 0.576 } 0.763 ± .257	0.320 0.528 0.528 } 0.459 ± .072	0.287 0.543 0.372 } 0.401 ± .142

[a]Standard is d_{10}-pyrene (m/z = 212).

The RMRs given here are to be regarded as typical values. Not only must they be determined for each instrument, but day-to-day variations are sometimes large enough to require daily calibration.

7.0 Quality Assurance Program

In addition to the validation procedures described above, an on-going quality assurance program is required to assure the data quality. Quality control (QC) procedures determine artifacts, losses, etc. through a system of blanks and controls. Quality assurance (QA) procedures monitor the execution of the procedure and check data interpretations and calculations.

7.1 Quality Control

7.1.1 Field Blanks and Controls

Prior to a field sampling trip, enough blanks and controls are prepared to equal 10% each of the anticipated number of field samples. Blanks consist of 50 ml of distilled water in the same type of sampling container as is used in the field. Controls consist of 50 ml of plasma spiked at 10-15 ng with the compounds listed in Table A-5. These blanks and controls are carried to the field and receive the same handling as the field samples. Workup and analysis of field blanks and controls is interspersed with the field samples on a regular basis. This method allows assessment of sample storage stability.

7.1.2 Procedural Blanks and Controls

7.1.2.1 Extraction Blanks

With each set of samples, a procedural blank is run. This consists of 5 ml of prepurged distilled water which is extracted under the same conditions as the samples. These blanks are designed to detect artifacts from dirty glassware, laboratory atmosphere intrusion, and other sources.

7.1.2.2 GC/MS Procedural Control

At the start of each working day, a mixture of 2,6-dimethylphenol, 2,6-dimethylaniline, and acetophenone (PA mixture) is analyzed to monitor the capillary GC column performance. This also serves to check the mass spectrometer tuning.

Field samples, field controls, field blanks, and procedural blanks are queued up for GC/MS analysis such that at least one QC sample is run each working day. In addition, a standard solution is analyzed each day to serve

Table A-5. SEMI-VOLATILE HALOGENATED HYDROCARBONS IN METHANOL SPIKING SOLUTION

Compound	Amt. spiked, ng
4-Chlorobiphenyl	13.2
Trifluralin	14.8
α-BHC	14.0
β-BHC	14.5
γ-BHC	15.2
4,4'-Dichlorobiphenyl	15.8
2,4,5-Trichlorobiphenyl	14.0
Heptachlor	13.6
Aldrin	14.8
Heptachlor epoxide	14.2
Endosulfan	13.1
Dieldrin	15.8
p,p'-DDE	11.6
p,p'-DDT	12.5
Endrin	11.5

as a procedural control and also to update the RMR value. Thus, in a typical working day, 4 field samples, 1 blank or control, and 1 RMR standard are run.

The Finnigan 3300 GC/MS is a quadrupole mass spectrometer which requires frequent tuning. Daily tuning is achieved using FC-43 and decafluorotriphenylphosphine (DFTPP).

7.2 Quality Assurance

7.2.1 Supervision and Monitoring of Activities

There are three levels of quality assurance (QA). The primary quality assurance is the person conducting the sampling and/or analysis. This person must be aware of their actions, observe events which may effect the data, and maintain appropriate records. At the second level, the chemist's supervisor monitors their daily activities, reviews the notebook, checks data and calculations, and assists in "troubleshooting" problems. At the tertiary level, a QA coordinator interviews all personnel on the project. The interviews cover the operations they perform (precisely), the data they obtain, a spot-check of their calculations, and any problems they have had.

7.2.2 Documentation

7.2.2.1 Chain of Custody

From the initial preparation of a sample container through reporting of the analytical results, each sample is accompanied by a chain of custody sheet. Each person signs in the time of receipt, operations performed, and transmittal of the sample. This record is important for tracing a contaminant, bad standard, or some other problem.

7.2.2.2 Sampling Protocol Sheets

When a sample is collected, a sampling protocol sheet is filled in which contains a discrete sample code which identifies project number, area, site, locations, trip number, sampling period, and sample type. Also included are sample times, volumes, addresses, meteorology, and other pertinent information. Where appropriate, a map is made to precisely identify the location.

7.2.2.3 Sample Log

Upon return from a sampling trip, each sample code is entered into a sample log book. This log is updated as samples proceed through workup and

analysis. Thus, at a glance, project personnel can tell the status of each sample and find out how many are at different stages in the analytical procotol.

7.2.2.4 GC/MS Log

Each sample run by GC/MS is logged into a notebook, detailing analysis conditions, where the data are archived, and what hardcopy data has been produced.

8.0 References

A1. Thompson, J. F., Analysis of Pesticide Residues in Human and Environmental Samples, A Compilation of Methods Selected for Use in Pesticide Monitoring Programs, Environ. Toxicol. Div., Health Effects Research Lab., USEPA, RTP, NC, December, 1974.

A2. Hines, J. W., R. Shapiro, E. Pellizzari and A. Schwartz, HRC and CC, submitted for publication (1978).

A3. Hines, J. R., R. Shapiro, A. Schwartz, and E. D. Pellizzari, HRC and CC, submitted for publication (1978).

A4. Sherma, J., Manual of Analytical Quality Control for Pesticides and Related Compounds, EPA-600/1-76-017, 1976, Table 7-1.

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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15. SUPPLEMENTARY NOTES

Project Officers are Vincent J. DeCarlo and Thomas E. Kopp

16. ABSTRACT

Fish and turtle (5 from Arkansas and 3 from Louisiana) caught downstream of the brominated organic chemical industry near El Dorado, AR were extracted, cleaned up, and analyzed by GC/MS for brominated organics using full scan and single ion monitoring electron impact GC/MS and negative ion chemical ionization GC/MS. PBBs ($C_{12}H_4Br_6$ and $C_{12}H_3Br_7$) were identified in one sample and several other brominated compounds were tentatively identified in several samples. Due to the high levels of interferences and very low levels of the compounds of interest, further identifications were impossible. The compounds were not quantitated, but levels appear to be much less than 1 ppm.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Brominated Organics Fish Turtles GC/MS PBBs GC/NICIMS Polybrominated biphenyls		

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