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JOB/PROJECT NO.: 484.4090

DATE: 4 May 1984

PERIOD COVERED:

TITLE: ANALYSIS OF DELAWARE RIVER PLANT SAMPLES

**AUTHORS: J. A. Giusti
F. D. Hileman
B. M. Hughes**

ABSTRACT: Water and sludge samples from the Delaware River plant were analyzed for specified chemical compounds. The research of these analyses are shown in this report.

TECHNICAL APPROVAL:

J. J. Brooks
J. J. Brooks

Senior Research Group Leader

APPROVED BY:

R. F. Ivory
R. F. Ivory

Environmental Science Center
Service Project Manager

APPROVAL DATE:

May 4, 1984

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MONS 220746

AUTHORS: J. A. Giusti, F. D. Hileman, B. M. Hughes
TITLE: ANALYSIS OF DELAWARE RIVER PLANT SAMPLES

REPORT NO.: MDA-475

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ACKNOWLEDGEMENT

Contributions of the following Dayton Laboratory personnel to this project are gratefully acknowledged:

Analyses: J. A. Giust
F. D. Hileman
B. M. Hughes
D. McKenzie
G. Thomas
C. Trang

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INTRODUCTION

Two water samples were received from the Delaware River plant for analysis of their possible Aroclor (PCB) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) concentrations. Two additional samples, one water and one sludge were received for the analysis of their possible metal concentrations by ion coupled plasma (ICP) spectroscopic analyses. The analytical results are shown in this report. Section one describes the TCDF analyses, section 2 the PCB analyses and section 3 the metal analyses.

SECTION 1 - ANALYTICAL RESULTS FOR 2,3,7,8 TCDF ANALYSIS

Water samples from the Delaware River Plant were received for the analysis of 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). The samples were labeled "PDA Well" and "PDA Blank Field Water". The samples were assigned Log number 1-84-02-29-01.

Samples were prepared by emptying the one liter bottle of water into a separatory funnel. The bottle is rinsed with 60 mL of methylene chloride (CH_2Cl_2) and this is added to the separatory funnel which is then shaken to extract the TCDF's into the CH_2Cl_2 . The CH_2Cl_2 is removed and saved and two additional CH_2Cl_2 extractions are made of the water and combined with the original CH_2Cl_2 extract. This extract contained a considerable amount of benzyl alcohol and benzaldehyde. These compounds were removed by solvent exchanging the CH_2Cl_2 to 15 mL methanol. The methanol was extracted three times with 10 mL portions of hexane and these hexane fractions were combined and partitioned against 50 mL of water followed by 100 mL of concentrated sulfuric acid. The hexane layer was dried over anhydrous sodium sulfate and concentrated to 2 mL.

The concentrate was applied to the top of a multiphase column containing (top to bottom) 2 g of silica, 4 g of silica plus 40% sulfuric acid, 1 g of silica, 2 g of silica plus 36% potassium hydroxide and finally 1 g of silica. The column was eluted with 50 mL of hexane with the eluant going directly onto a column containing 2.5 grams of Woelm basic alumina. This column was first eluted with 10 mL of 2% CH_2Cl_2 /hexane to remove PCB's and this fraction was discarded. The column was then eluted with 15 mL of 50% CH_2Cl_2 /hexane and this fraction was saved and concentrated to 10 μL in a keeper of dodecane and submitted for GC/MS analysis.

The GC/MS analysis was carried out on a Hewlett Packard 5985B GC/MS system with the gas chromatographic separations on a 60 meter SP-2330 capillary column. The mass spectrometer was operated in

the selected ion monitoring mode following ions characteristic of the TCDF's and the surrogates that were used.

Quantitation was achieved by ratioing the amount of 2378-TCDF in the sample to the amount of $^{13}\text{C}_{12}$ -2378-TCDF which had been added to the water at the very outset of the extraction procedure. This isotopically labeled surrogate provides for accurate quantitation even though the actual recovery of the TCDF's can be quite variable.

The results of the analyses are shown in Table 1. Included in the table are the results from the spiking studies in which native (non-isotopically labeled) TCDF was added to the samples.

**ANALYSIS OF WATER SAMPLES
FOR 2,3,7,8-TETRACHLORODIBENZO FURAN**

<u>Sample</u>	<u>ppt 2378-TCDF found</u>	<u>ppt 2378-TCDF added</u>
PDA Well	92	-
PDA Well (Rep)	100	-
PDA Well (Spike)	125	25
PDA Blank Field Water	ND*	-
PDA Blank Field Water (Spike)	2.3	2.5
D & J Water Lab Blank	ND	-
Method Detection Limit	1	-

*ND = none detected at the Method Detection Limit

SECTION 3

TITLE: ICP-AES ANALYSIS OF DELAWARE RIVER SAMPLES

DATE: 9 MARCH 84

RECORD NUMBER: 1-84-02-29-01

PROJECT NUMBER: 484.40911

NOTEBOOK REFERENCE: MONSANTO 2463927

TITLE: ICP-AES ANALYSIS OF DELAWARE RIVER WATER SAMPLES

BACKGROUND

TWO WATER SAMPLES WERE RECEIVED FROM DELAWARE RIVER FOR A TRACE METAL SCAN BY ICP-AES. THE TWO SAMPLES RECEIVED WERE LABELED: PDA WELL AND PDA SLUDGE.

PROCEDURE:

100ML OF EACH SAMPLE WAS DIGESTED WITH HOT HNO₃ AS OUTLINED IN: EPA METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES PART 4.1.3 TOTAL RECOVERABLE METALS

AFTER DIGESTION, THE TREATED SAMPLE WAS RETURNED TO ITS ORIGINAL VOLUME.

INSTRUMENTAL METHOD:

THE DIGESTS AND BLANK WERE ANALYSED BY ICP-AES USING DIRECT ASPIRATION.

ANALYTICAL RESULTS:

TABLE #1 (VALUES IN PPM)

	PDA WELL	PDA SLUDGE
AL	52	356
B	<0.5	<0.5
BA	0.5	1.0
BE	<0.5	<0.5
CA	68	87
CD	<0.5	<0.5
CO	<0.5	0.9
CR	<0.5	<0.5
CU	<0.5	<0.5
FE	610	2250
MG	69	135
MN	38	71
MO	<0.5	<0.5
NI	0.9	4.0
PB	<0.5	<0.5
SN	1.1	2.1
TI	<0.5	<0.5
V	0.5	1.9
ZN	4.6	7.2

TABLE #2
RESULTS OF STANDARD REFERENCE MATERIAL ANALYSIS
ELEMENT(% OF TRUE VALUE AS DETERMINED BY ANALYSIS)

AL(104%)	B(115%)	BA(93%)	BE(93%)
CD(107%)	CO(102%)	CR(96%)	CU(95%)
FE(95%)	MN(98%)	MO(133%)	NI(102%)
PB(105%)	TI(121%)	V(102%)	ZN(105%)

DISCUSSION OF RESULTS

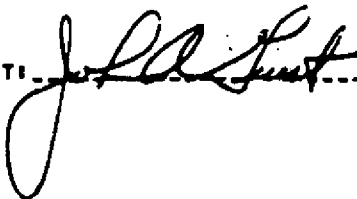
BOTH SAMPLES(PDA WELL AND PDA SLUDGE) CONTAINED SIGNIFICANTLY HIGH CONCENTRATIONS OF IRON, MAGNESIUM, MANGANESE AND ZINC. DUE TO THE SPECTRAL INTERFERENCES GENERATED BY THE HIGH CONCENTRATIONS OF THESE ELEMENTS, THE ANALYSIS OF THESE ELEMENTS IN THESE SAMPLES WAS NOT ACCURATE.

TRATIONS OF THESE ELEMENTS THE VALUES FOR ALL OTHER ELEMENTS WILL BE EITHER ENHANCED OR SUPPRESSED DEPENDING UPON THE NATURE OF THE SPECTRAL INTERFERENCE. THEREFORE, THE VALUES REPORTED FOR ALL ELEMENTS WITH THE EXCEPTION OF FE, MG, MN, AND IN CAN BE CONSIDERED AS SEMI-QUANTITATIVE ONLY.

QA/QC INFORMATION

DUE TO THE FACT THAT THE REQUESTER (ED JAMRO) AT DELAWARE RIVER ASKED THAT THE SAMPLES BE TURNED AROUND AS QUICKLY AS POSSIBLE, THE FULL SET OF QA/QC SAMPLES (10... SPLITS AND SPIKES) WERE NOT GENERATED DURING THE ANALYSIS IN AN EFFORT TO SATISFY ED JAMRO'S REQUIREMENTS FOR THE QUICKEST TURN-AROUND POSSIBLE.

ANALYST: _____

A handwritten signature in cursive script, appearing to read "J. A. Lunt", is written over a horizontal dashed line.

SECTION 2
ANALYSIS REPORT
FOR AROCLOR 1248

DATE: March 26, 1984

LOG NUMBER: 1-84-02-29-01

PROJECT NO: 484.40918

TO:

Report sent via Federal Express to:

Mr. Ed Janso
Monsanto Delaware River Plant
Rt 130
Bridgeport, N. J. 08014

FROM:

Environmental Sciences Center
Monsanto Company/Darton Laboratory
1515 Nicholas Road
Darton, Ohio 45418

Phone No: (513) 268-3411

Title: Analysis of Two Water Samples for Aroclor 1248

Standard Sampling Method No(s): N/A

Standard Extraction Method No(s): PCEX02

Standard Analysis Method No(s): ECAN02

Final Report File No(s): A40918

Table File No(s): B40918, C40918

Two water samples were analyzed for Aroclor 1248. No Aroclor 1248 was detected in the PDA-Water Blank Sample with a level of detection of 1 ug/L. Two aliquots of the sample labelled PDA-Well were analyzed. One contained sediment and the second contained no visible amounts of sediment. The results of analysis for Aroclor 1248 in these two samples are shown in Table 1. Chromatograms of the Aroclor 1248 standard (1 ug/mL) and the two extracts from the PDA-Well sample are shown in Figure 1. Since there is a difference in concentration of approximately one order of magnitude between the samples this one well sample was centrifuged and reanalyzed in an effort to obtain accurate values for Aroclor 1248 in a sample which has no sediment. The results of analysis of a sample containing sediment and a sample which had been centrifuged are shown in Table 2. Figure 2 shows comparison chromatograms of these two samples and an Aroclor 1248 standard. As can be seen, the Aroclor concentration in the centrifuged water sample is approximately five times lower than the clear sample results shown in Table 1. Therefore the concentration for the clear sample probably shows that some sediment was also in this latter sample.

It appears that water samples should be analyzed centrifuged and not centrifuged in order to obtain accurate values for Aroclor concentrations which are present as dissolved PCBs in water, and also which may be present as PCBs adsorbed on sediment which may be suspended in water samples.

ANALYST(S): B. Mason Hushes, David McKenzie, Chi Tran

ANALYST APPROVAL: B. M. Hushes

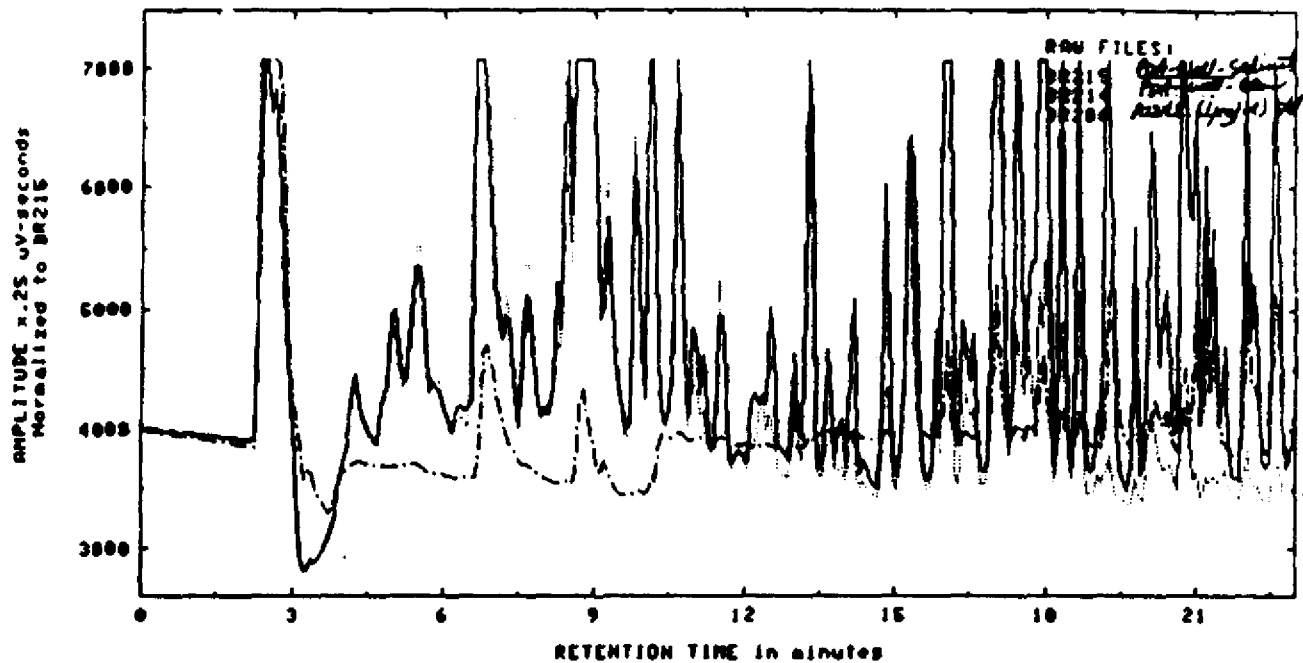


Figure 1. Comparison of replicate GC/EC chromatograms for
 water samples and for Aerosol 1248 standard

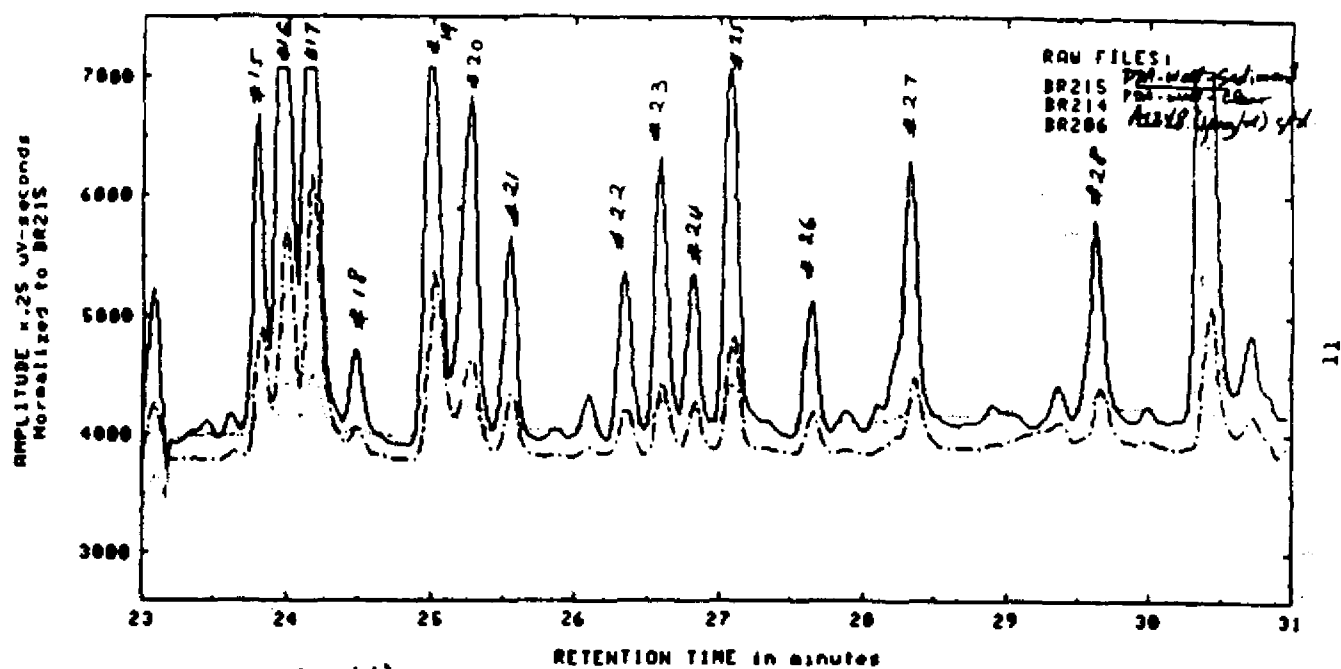


Figure 2 (cont'd)

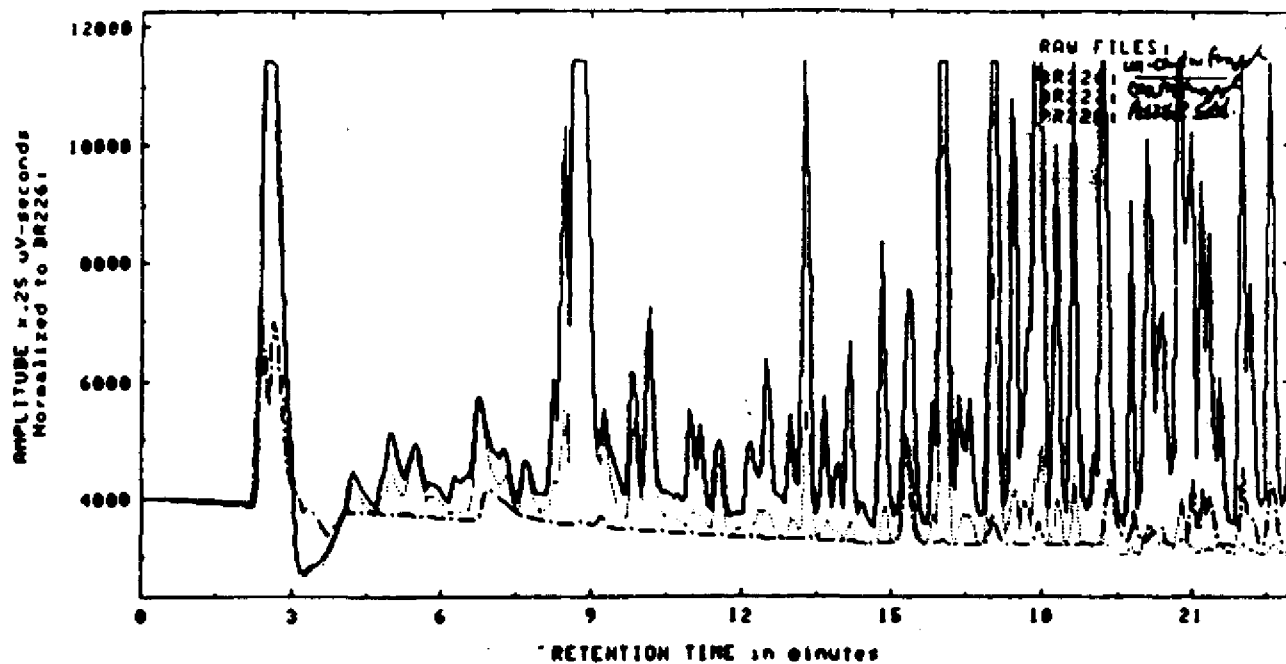


Figure 2. Comparison of capillary GC/EC chromatograms of centrifuged and uncentrifuged water sample and an Amtech 1248 Standard

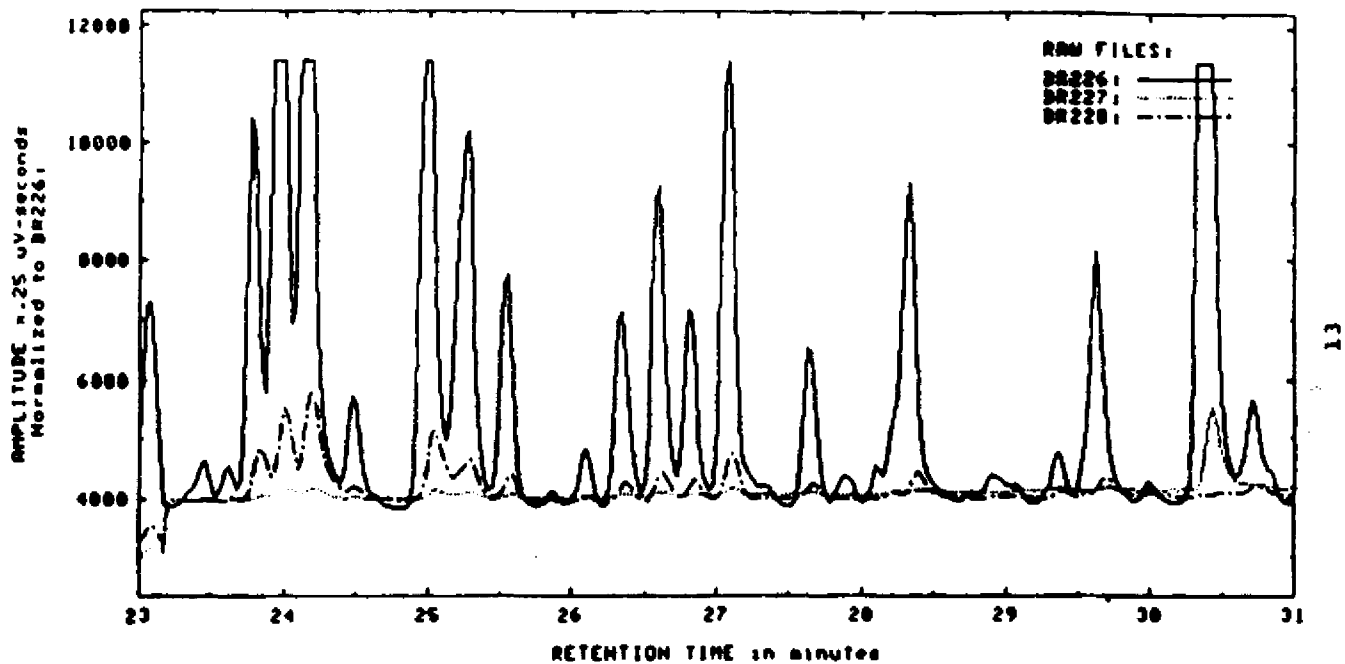


Figure 2 (cont'd).

TABLE 1. Concentration of Aroclor 1248 Measured in two Aliquots of PDA-Well Samples

ESC Project No: 484.40918

Date: March 6, 1984

SAMPLE IDENTIFICATION					
Aroclor 1248 Concener Number	PDA-Well Clear		PDA-Well Sediment		Aroclor 1248 STD (µg/ml)
	Area	A1248 Conc. (µg/g)	Area	A1248 Conc. (µg/g)	Area
015	2359	.18	30683	2.36	13002
016	6257	.24	70552	2.69	26212
017	7095	.20	83627	2.33	35905
018	-	-	8406	3.04	2768
019	5420	.22	61570	2.54	24231
020	3974	.26	48527	3.20	15179
021	1335	.20	21167	3.11	6801
022	1733	.35	17484	3.59	4866
023	2586	.33	28900	3.71	7780
024	1078	.21	15962	3.09	5157
025	3852	.33	39988	3.46	11561
026	1107	.28	13643	3.44	3968
027	2432	.23	37037	3.50	10580
028	1481	.22	24616	3.64	6767
Average A1248 Concentration (µg/g)		.25		3.12	
ESC Extraction Method	PCEX02		PCEX02		PCEX02
Sample Amt extracted (g)	10		10		-
Extract Dilution	1110		1110		111
ESC Extract No.	PCB325		PCB326		A1248
Process File Name	BP214		BP215		BP206
=====					
TABLE FILE NO: 840918					

TABLE 2. Concentration of Aroclor 1248 Measured in two Aliquots of PDA-Well Samples

ESC Project No: 404.40918

Date: March 7, 1984

SAMPLE IDENTIFICATION					
Aroclor 1248 Condenser Number	PDA-Well Centrifused		PDA-Well Not Centrifused		Aroclor 1248 STD (1ug/ml)
	Area	A1248 Conc. (ug/e)	Area	A1248 Conc. (ug/e)	Area
015	-	-	82104	.76	10494
016	1087	.050	170302	7.96	21397
017	1105	.036	202477	4.61	30634
018	-	-	28895	11.77	2456
019	-	-	145454	7.58	19212
020	-	-	110224	8.43	13071
021	-	-	50384	8.95	5629
022	-	-	42474	11.67	3641
023	-	-	71616	12.42	5768
024	-	-	44083	10.83	4070
025	-	-	108025	11.63	9288
026	-	-	33089	11.03	2999
027	-	-	89343	16.84	5306
028	-	-	65363	15.67	4171
Average A1248 Concentration (ug/e)		.043	10.88		

ESC Extraction Method	PCEX02		PCEX02		PCEX02
Sample Amt extracted (e)	10		10		-
Extract Dilution	111		111		111
ESC Extract No.	PCB332		PCB331		A1248
Process File Name	BP227		BP226		BP228
=====					
TABLE FILE NO: C40918					

DETAILED EXPLANATION OF TABLES

In an effort to streamline reports generated by ESC on PCBs present in a wide variety of materials, using a wide variety of techniques, Standard Extraction Methods (SEMs) and Standard Analysis Methods (SAMs) have been developed which can be easily interfaced with each other. An abbreviated form of these SEMs and SAMs have been stored on the Hewlett-Packard 3357-LAS laboratory automation system used by ESC. In an effort to communicate these details with customers of ESC, this information is supplied with each PCB analysis. However, many projects involve a very small number of samples which are not necessarily the same matrix. Therefore, major information on the technical details of an analysis are presented in tabular form within the same table which reports the data.

Each table includes a general title, ESC Project Number and Date on which the table was generated. The sample identification is the customer identification which was on the sample bottle. The next section of the table gives results for the particular analyte listed. For Arcelor formulations, the formulation is identified either visually or from ESC developed data analysis programs. The concentration of the formulation is calculated from the average value of the Arcelor formulation, based upon the analysis of a number of PCB isomers. The number of isomers used in this calculation is given as "No. of Values" and the range of Arcelor concentrations for this number of PCB isomers is given by "Rng of Values". The standard deviation and X relative standard deviation for this number of determinations of the Arcelor formulation are given in the following two lines of the tables.

The next section of the table deals with quality control used in each sample analysis. The surrogate spiking compound which is added to the sample before extraction and analysis is listed, along with its amount and X Recovery measured for each sample. In cases where PCB concentrations are very high and thus require extract dilution, no effort is made to quantify this compound. This could be done if ESC knows that this data is important, but typically 50 ug/g is the important level to quantify accurately so that surrogate data for concentrations larger than this value, from a regulatory standpoint, are not important.

The next section documents how each sample was extracted and analyzed. The ESC Extraction Method, amount of sample extracted, extract final volume, extract dilution factor, ESC extract number and the computer data file in which the processed data is stored are given in this section. The last section gives a brief description of abbreviations or gives any footnotes that give additional information about specific samples.

This table format is both compact and precise. It was developed in an attempt to quickly and accurately generate data which the customer can quickly and accurately evaluate. If there are any suggestions concerning this format, please contact me at extension 396.

DESCRIPTION STORED IN TBEX01PH

The following pages describe Standard Extraction Methods and Standard Analysis Methods used for this project.

ESC Standard Extraction Method (SEM)
TITLE: PCBs in Various Matrices

ESC Standard Extraction Method No:
PCEX01

MATRIX(ES):

Still bottoms, soils, beef fat,
beef serum, whole milk, beef
feces

TYPICAL SAMPLE
SIZE
(g)

TYPICAL EXTRACT
VOLUME
(ml)

0.5 - 5.0

1 - 10

TYPICAL ANALYTES: Aroclors 1232, 1242,
1248, 1254, 1260, 1262, trichloro-
biphenyl isomers through octachloro-
biphenyl isomers

ESC Standard Analysis Method Nos:
ECAN01, ECAN02, MSAN03

INTERFERENCES: Any electron capturing
species in the retention time region
of trichlorobiphenyl isomers through
octachlorobiphenyl isomers for ECAN01
and ECAN02. Any species in the
appropriate retention time region
which give the same relative charac-
teristic mass responses as PCB isomers
for MSAN03.

TYPICAL
SURROGATES

TYPICAL
RECOVERIES (%)

pentachlorobenzene 50 - 120
2,4,6-trichloro-
biphenyl 50 - 120

APPARATUS AND MATERIALS:

Burdick and Jackson hexane, benzene and methylene chloride for sample
extraction.
Concentrated sulfuric acid for sample digestion or sample clean-up.
Silica gel columns impregnated with potassium permanganate, sulfuric acid,
and potassium hydroxide.
Activated basic alumina.
Disposable glassware.

LIMITATIONS: Method applies only to matrices which do not contain non-hydro-
lizable electron capturing species in the trichlorobiphenyl through octa-
chlorobiphenyl isomer retention time region for EC detection methods.

SAFETY PRECAUTIONS: See PCB handling protocols in laboratory safety manual.

DATES OF METHOD CREATION AND UPDATES: 10/25/83, 2/3/84

EBC Standard Analysis Method (SAM)
TITLE: Aroclor Formulations in Solvents

EBC Standard Analysis Method No:
ECAN02

ANALYTICAL INSTRUMENT AND MODE OF OPERATION: HP-5880 Capillary GC/EC interfaced to an HP-3357-LAS Laboratory Data System

TYPICAL ANALYTE	TYPICAL INSTRUMENT LEVEL OF DETECTION (LOD) (ug/ml)	TYPICAL PRECISION @ 10X LOD (%)	TYPICAL ACCURACY @ 10X LOD (%)
Aroclor formulations 1232, 1242, 1248, 1254, 1260, and 1262	0.1	30	30

INTERFERENCES AND LIMITATIONS: Any electron capturing species in the retention time region of trichlorobiphenyl through octachlorobiphenyl isomers are potential interferences. Exact retention times of most likely PCB isomers can be obtained from the analysis of Aroclor 1248, Aroclor 1254 or Aroclor 1260 formulations.

CHROMATOGRAPHIC COLUMN: 30-meter fused silica J&W DB-5 (0.25 um) with wide bore (0.32mm).

COLUMN TEMPERATURE PROGRAM: 130(1)/4/300

INJECTION TYPE: Splitless

CALIBRATION AND STANDARDIZATION: Use internal standard quantitation technique and calibrate instrument response factors from authentic Aroclor formulation standards. Use a minimum of 10 PCB isomers for the determination of formulation identity and quantity.

CALCULATIONS: Formulation concentration = (isomer area)/(isomer RRF)

where: RRF is the relative response factor for the appropriate PCB isomer in a given formulation. Formulation concentration is obtained from the average of at least 10 such calculations.

SAFETY PRECAUTIONS: See PCB handling protocols in laboratory safety manual.

DATES OF METHOD CREATION AND METHOD UPDATES: 10/23/83, 2/3/84

The following pages describe Analytical Request Information generated for this project.

NRC ENVIRONMENTAL SCIENCES CENTER

ANALYSIS REQUEST

DATE: FEBRUARY 29, 1984

LOG NO: 1-84-02-29-01

REQUESTER:

DELAWARE RIVER/IVORY

PROJECT NO:

484,40918

REPORT RESULTS TO: FILES/NEES, IVORY, BROOKS

ANALYSIS REQUESTS SENT TO: FILES, IVORY, OJUST, HILEMAN, MCHES, BROOKS

SAMPLE PICKUP BY: D. MCKENZIE

SAMPLE LOCATION:

SAMPLE IDENTIFICATION	SAMPLE DESCRIPTION FOR 4 SAMPLES NUMBER OF BOTTLES	NUMBER(S)
PDA - WATER BLANK	5	PCB324
PDA - WELL	4 (clear)	PCB325
	(sediment)	PCB326
	(centrifused)	PCB332
	(not centrifused)	PCB331
PDA - WELL FOR ICAP METALS EXCEPT H0	1	
PDA SLUDGE FOR ICAP METALS EXCEPT H0	1	

RECORDED BY: P. HUPP

REQUIRED ANALYSES: PCB, DIBENZOFURANS, METALS (EXCEPT H0)

ANALYTICAL TECHNIQUES:

	DATE COMPLETED		DATE COMPLETED
X GC/EC (10)	3/26/84	X ICP ()	----
		X GC/MS (34)	----

QUALITATIVE: YES

SEMIQUANTITATIVE:

QUANTITATIVE: YES

REQUIRED QA/QC:

COMPLETION DATE REQUESTED: Immediately.

COMMENTS: PCB results phoned and sent to Ed Jamro/Delaware River Plant.

SAMPLE DISPOSITION:

X HOLD FOR 30 DAYS

SAFETY PRECAUTIONS: May contain PCBs, chlorinated dibenzofurans and Hs.

ANALYSIS REQUEST FILE NAME: AA40901L1