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REPORT NO.: MDA-647

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TITLE: ANALYSES OF SOIL & OIL SAMPLES FOR PCB's AND PCDD's

AUTHORS: F. D. Hileman
B. M. Hughes

ABSTRACT: Soil and oil samples were analyzed for possible concentrations of PCB's and PCDD's. The analyses performed and the results obtained from these analyses are shown in this report.

TECHNICAL APPROVAL:
P. L. Sherman
Sr. Research Group Leader

APPROVED BY:
R. F. Ivory
Environmental Sciences Center
Service Project Manager

APPROVAL DATE: 7-31-85

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ACKNOWLEDGEMENT

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

Analyses: F. Hileman
M. Hughes
D. McKenzie
C. Trang

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SECTION A

ANALYSIS FOR POLYCHLORINATED DIBENZO-P-DIOXINS

ANALYSIS OF RESIDUES AND SOILS FOR POLYCHLORINATED DIBENZO-P-DIOXINS

INTRODUCTION

Six samples were received for the analysis of polychlorinated dibenzo-p-dioxins (PCDDs). There was one oily residue sample labelad "Q1042-1,GS-01-00," one solid residue labelad "Q1042-1,R0-01-00" and four soils labeled "Q1042-1,GS-01-01" through "Q1042-1,GS-04-01". The samples were assigned log number 1-85-07-11-01. For quality assurance purposes Method #07-QAQC-R3 was followed. This method requires that for every set of samples of the same matrix type (in this case there were three matrices) a replicate, a low level spiked sample, a high level spiked sample and a method blank must also be analyzed.

PREPARATION AND ANALYSIS

The residue samples (both oil and solid) were weighed out and then dissolved in 40 mL of hexane. The hexane was then repeatedly partitioned against 30 mL portions of concentrated sulfuric acid until the sulfuric acid layer remained clear and colorless. The hexane was then partitioned against 30 mL organic free water to remove any residual sulfuric acid. The water was then removed and the hexane was dried over anhydrous sodium sulfate and concentrated to 5 mL.

The soil samples were first weighed and then placed in a bottle with anhydrous sodium sulfate to dry the soil. This soil was then extracted with 150 mL of hexane and 15 mL methanol with shaking for 2 hours. The extract was decanted off and partitioned against 30 mL of water to remove the methanol. The hexane was then partitioned against concentrated sulfuric acid in a manner similar to the residue samples.

The hexane concentrate was then placed on a column made from a 25 mL disposable pipet packed with (top to bottom) 2 g of silica, 4 g of silica plus 40% sulfuric acid, 1 g silica, 2 g silica plus 36% potassium hydroxide and 1 g silica. The column was eluted with 40 mL of hexane and this eluant was dried over sodium sulfate and concentrated to 2 mL.

The concentrate was then placed upon the head of a column made from a 10 mL disposable pipet containing 2.5 g of Woelm basic alumina. This column was first eluted with 10 mL of 2% methylene chloride/hexane (v/v) mixture and this fraction discarded. An additional elution was made with 15 mL of a 50% methylene chloride/hexane (v/v) mixture to elute the PCDDs from the column.

MONS 023554

The eluants from the Woelm columns had 50 uL of dodecane, containing tribromobiphenyl as an internal standard, added to them as a keeper and were then concentrated to 50 uL under a gentle stream of purified nitrogen and submitted for GC/MS analysis. The GC/MS analysis was conducted on a Hewlett/Packard 5987 instrument. The mass spectrometer was operated in the selected ion monitoring mode analyzing for ions characteristic of the native (unlabeled) PCDDs and the internal standards.

RESULTS

The results of the analyses are shown in Tables 1 through 3. Note that each different matrix (two types of residues and soil) were run with their own quality control samples. The analysis of the soil samples was straight forward with good recoveries for all the PCDDs with the exception of the lower chlorinated congeners (Cl-1 - Cl-3). Sample GS-04-01 showed the low level presence of both hepta and octachlorodibenzp-p-dioxins which is very likely due to low level pentachlorophenol contamination.

The results from the residues showed highly variable recoveries for the PCDDs. This comes from the chemical nature of these residues and the work up procedures that were used to clean up the samples (i.e. the extensive partitions against concentrated sulfuric acid). In spite of these problems the important fact was that no PCDDs in the Cl-4 to Cl-6 classes (the ones of most concern) were observed in these residues at the specified detection limits. Again, in sample GS-01-00 some octachlorodibenzo-p-dioxin was observed most likely indicative of pentachlorophenol contamination.

MONS 023555

Table 1. ANALYSIS OF PCDDs in SOIL

ng PCDDs/gm Soil (ppb)

Sample	CL-1	CL-2	CL-3	CL-4	CL-5	CL-6	CL-7	CL-8
GS-01-01	ND	ND	ND	ND	ND	ND	ND	ND
GS-01-01 Replicate	ND	ND	ND	ND	ND	ND	ND	ND
GS 02-01	ND	ND	ND	ND	ND	ND	ND	1.1
GS-03-01	ND	ND	ND	ND	ND	ND	ND	ND
GS-04-01	ND	ND	ND	ND	ND	ND	1.0	5.3
BLANK	ND	ND	ND	ND	ND	ND	ND	ND
MDL	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
S. LEVEL	2.5	2.5	2.7	2.0	2.4	2.3	2.5	2.0
GS-03-01 LOW SPIKE	0.8	1.6	1.7	1.5	1.9	1.9	2.2	1.8
% REC	32	64	63	75	80	80	88	90
S. LEVEL	25	24	27	19	24	23	25	20
GS-02-01	7.5	14	17	16	20	21	24	18
% REC	30	58	63	84	83	91	96	90

% REC - percent recovery of spike
MDL - method detection limit
ND - none detected at method detection limit
S level - spike level (ppb)

MONS 023556

Table 2. ANALYSIS OF PCDDs IN OIL RESIDUE

ng PCDDs/gm Residue (ppb)

Sample	CL-1	CL-2	CL-3	CL-4	CL-5	CL-6	CL-7	CL-8
RO-01-00	ND	ND	ND	ND	ND	ND	ND	ND
RO-01-00 REPLICATE	ND	ND	ND	ND	ND	ND	ND	ND
BLANK	ND	ND	ND	ND	ND	ND	ND	ND
MDL	>24	>24	>26	1.0	1.0	1.0	1.0	2.0
$ LEVEL	2.4	2.4	2.6	1.9	2.3	2.2	2.4	1.9
RO-01-00 LOW SPIKE	ND	ND	ND	1.3	1.8	1.3	2.5	13
% REC	-	-	-	68	78	59	104	-
$. LEVEL	24	24	26	19	23	22	24	19
RO-01-00 HIGH SPIKE	ND	2.9	ND	13	5.3	3.6	9.9	49
% REC	-	-	-	68	23	16	41	-

MDL - method detection limit
ND - none detected at method detection limit
$ level - spike level (ppb)
% REC - percent recovery of spike

MONS 023557

Table 3. ANALYSIS OF PCDDs IN SOLID RESIDUE

ng PCDDs/gm Residue (ppb)

Sample	CL-1	CL-2	CL-3	CL-4	CL-5	CL-6	CL-7	CL-8
GS-01-00	ND	ND	ND	ND	ND	ND	1.6	3.2
GS-01-00 REPLICATE	ND	ND	ND	ND	ND	ND	2.2	4.7
BLANK	ND	ND	ND	ND	ND	ND	ND	ND
MDL	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$ LEVEL	4.8	4.8	5.2	3.8	4.6	4.4	4.8	3.8
GS-01-00 LOW SPIKE	1.8	2.8	3.2	4.2	5.8	6.5	8.5	8.8
% REC	38	58	62	110	126	148	138	128
$. LEVEL	49	48	53	39	47	45	49	39
GS-01-00 HIGH SPIKE	14	23	33	46	81	81	87	65
% REC	29	48	62	118	172	180	174	156

MDL - method detection limit
ND - none detected at method detection limit
$ level - spike level (ppb)
% REC - percent recovery of spike

MONS 023558

SECTION B

ANALYSIS FOR POLYCHLORINATED BIPHENYLS

ANALYSIS REPORT

DATE: 7/30/85

LOG NUMBER: 1-85-07-11-01 PROJECT NO: 760.18 - 327

TO: MIC/Pat Hyland

FROM: Environmental Sciences Center
Monsanto Company/Dayton Laboratory
1515 Nicholas Road
Dayton, Ohio 45418

Phone No: (513) 268-3411

Title: Analyses for PCBs in MIC Soil and Oil Samples

Standard Sampling Method No(s): Samples supplied by customer.

Standard Extraction Method No(s): PCEX21 and PCEX14

Standard Analysis Method No(s): ECANO2 and MSANO3

Final Report File No(s): C32718

Table File No(s): D32718 and E32718

Five soil samples and one oil sample were analyzed for PCBs. The soils were subjected to Standard Extraction Method PCEX21 and Standard Analysis Method ECANO2. None of the soil samples received contained PCBs above the limit of detection (1 ug/g). Results of soil analyses are located in Table 1.

The oil sample was subjected to Standard Extraction Method PCEX14 and Standard Analysis Method MSANO3. Protocols developed for Incidental PCB Analyses were utilized. Results of the oil analysis are located in Table 2. No Cl-biphenyl or Cl3-biphenyl congeners were detected above 10 ug/g and no other PCB congener was detected above a concentration of 1 ug/g.

Also included in this report are:

1) Detailed explanations of the tables generated.
2) Raw data documentation.
3) QA/QC spiking information for the oil sample.
4) Standard Extraction and Analysis Methods used for this project.
5) Analytical Request Information generated.
6) A copy of ESC/DAS GLP Manual which explains quality control procedures utilized by ESC.

ANALYST(S): B. Mason Hughes, Chi Trang, and David McKenzie

ANALYST APPROVAL: _____

Time Stamp - (850730.1325)

TABLE 1. Summary of PCB Concentrations and QA/QC for NIC Soil Samples.

ESC Project No: 760.18 - 327 Date: July 30, 1985

Sample I.D.	Surrogate Recoveries(%Recovery)		PCB Concentration (ug/g)
	CL5-benzene	2,4,6-CL3-biphenyl	
NIC, Q1042-1 65-01-01	100	106	ND(a)
NIC, Q1042-1 65-01-01 (DUP)	104	112	*
NIC, Q1042-1 65-02-01	100	102	*
NIC, Q1042-1 65-03-01	106	104	*
NIC, Q1042-1 65-04-01	101	106	*
NIC, Q1042-1 65-01-00	332	358	*
NIC, Q1042-1 65-01-00 - Dup	122	162	*
Dayton Soil Blank	103	109	*

Native Spiking Data(b)

	Amount A1254 Spiked (ug/g)	Amount Detected (ug g
Dayton Soil Blank + LS	1.1	1.4
Dayton Soil Balnk + HS	10.3	12.7

Explanation of Table: Limit of detection (LOD) = 1.0 ug/g
Duplicate analysis = DUP
LS = low level native spike
HS = high level native spike

Footnote(s): a - ND = not detected at the LOD.
b - See UAG/SLP manual for quality control criteria.

TABLE FILE NO: D22718:MH

Time Step 4 (850730.1341)

Table 2. Results of Incidental PCB Analyses.

Project No: 760.18-327 Date: July 30 1985

	Sample Identification		
	Q1042-1 RO-01-00	Q1042-1 RO-01-00(dup)	Method Blank
Congener Class	Analytical Method	LOQ(a) (ug/g)	Concentration (ug/g)		
CL1-BP	HSA#03	10(E)	BQ(b)	BQ	BQ
CL2-BP	"	1(M)	"	"	"
CL3-BP	"	10(E)	"	"	"
CL4-BP	"	1(M)	"	"	"
CL5-BP	"	"	"	"	"
CL6-BP	"	"	"	"	"
CL7-BP	"	"	"	"	"
CL8-BP	"	"	"	"	"
CL9-BP	"	"	"	"	"
CL10-BP	"	"	"	"	"

Surrogate Spiking Compound	Amount Added(ug/g)	Recovery (%)
3,4,3',4'-CL4-BP	1.0	Could not quantitate due to large interferences.

Documentation

ESC Extraction Method	PCEX14	PCEX14	PCEX14
Date of Extraction	7/19/85	7/18/85	7/18/85
Sample Amount Extracted (g)	0.9820	0.9640	-
Extract Final Volume (ml)	1.0	1.0	1.0
Extract Dilution	none	none	none
ESC Extract or Sample Number	PCB-1404	PCB-1405	PCB-1408
Date of GSC/MS Analysis	7/19/85	7/19/85	7/19/85
MS FRN	>L0356	>L0357	>L0358

Footnotes:

(a) LOQ - Limit of Quantitation in ug/g. Signal-to-noise ratio is greater than 10 when this amount is analyzed using the above referenced Analytical and Extraction Methods. The following letters indicate how this value was determined:
E - estimated from PCB congener standard analyzed under the same conditions.
M - measured from native spiking of sample matrix.
S - estimated from surrogate spiking of sample matrix.
V - measured in validation experiments of similar sample matrix.

(b) BQ - Not Quantitatable. The congener concentration is below the LOQ value.

Table stored in file: E32718:MM:59

Analyst(s): B. Mason Hughes, David McKenzie and Barbara Williams

Analyst Approval: B. Mason Hughes

The Following Page is a Detailed Explanation of Tables Generated for this Project.

DETAILED EXPLANATION OF TABLES

In an effort to streamline reports generated by ESC on a wide range of analytes in a wide range of matrices, using a wide range of extraction and analysis techniques, modularized Standard Extraction Methods (SEMs) and Standard Analysis Methods (SAMs) have been developed. An abbreviated form of these SEMs and SAMs have been stored on the Hewlett-Packard 3357-Laboratory Automation System used by ESC. In a effort to communicate these details with customers of ESC, this information is supplied with all analyses. This information is supplied as supplemental information in this analysis report and the appropriate SEMs and SAMs are referenced in each data table. A large amount of documentation is also included in these tables. The following paragraphs describe some of the important information included.

Each table includes a general title, ESC Project Number and Date on which the table was generated. This information should be referenced if questions arise concerning the report. Below the date, the customer identifications, which were supplied on sample bottles, are listed. The next section of the table gives results for various analytes. The Level of Detection (LOD) and the actual concentration found (if greater than the LOD) are given for each analyte. It is important to understand how the LOD was determined. PCB levels of detection are determined by actually spiking the matrix at the instrument level of detection. The recoveries of these native spiking studies are normally supplied in separate QA/QC tables. This type of LOD determination is referenced with footnote H. For other analytes, there are several methods of determining the LOD for a particular analysis. The method used is given in the table footnotes. If analyses have been requested for all chromatographable materials which may be present in a particular sample, there may be components which cannot be identified from their mass spectra. In this case, the response factors used for the calculations of LOD and concentrations are based either on Surrogate or Internal Standard response factors. If the analytes are identified, but analytical standards are not available at the time of analysis, their LODs and concentrations may also be determined from Surrogate and Internal Standard response factors. When Surrogate or Internal Standards are used for estimating the LODs and concentrations of analytes, footnote S is referenced. Finally, if standards of analytes are analyzed using conditions identical to those used for the extract analysis, LODs and concentrations of analytes can be estimated from these standards analyses. This type of calibration is referenced with footnote E.

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 % 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 these data are 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. For other analytes, surrogate recoveries are used to estimate recoveries of the analytes of interest. Ideally, surrogate compounds should be chemically identical to the analytes of interest. However when analytes cannot be identified from their mass spectra, or when isotopically labelled analytes are unavailable, the surrogate compounds used in the study are assumed to partition between the matrix and the extracting solvent in a manner similar to the analytes of interest.

DETAILED EXPLANATION OF TABLES (cont'd)

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 for each sample. Following this section is a brief description of abbreviations and a summary of 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 Mason Hughes at extention 396.

DESCRIPTION STORED IN TDEXO2:MH:22 Time Stamp - <850412.0923>

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DETAILED EXPLANATION OF INCIDENTAL PCB TABLES

In an effort to streamline reports generated by ESC on incidental 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 has been stored on the Hewlett-Packard 3357-LAS computer system used by ESC. In an effort to communicate these details with customers of ESC, this information is supplied with each incidental PCB analysis. However, many projects involve a very small number of samples which are not necessarily the same matrix. Therefore, to reduce costs of generating reports for these small projects, 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 PCB congener class listed. The level of quantitation (LOQ) using the Analytical and Extraction Methods shown in the table, is given for each congener class. This LOQ is determined in one of four ways and is described in the table footnotes.

The next section of the table deals with quality control used in each sample analysis. The surrogate spiking compound (if used) which is added to the sample before extraction and analysis, is listed, along with the amount added and % Recovery measured for each sample. The final section before the footnotes deals with how each sample was extracted and data documentation. The ESC Extraction Method, Date of Sample Extraction, Amount of Sample Extracted, Extract Final Volume, Extract Dilution and ESC Extract or Sample Number give critical extraction details of the analysis. The date of CGC/MS analysis and the mass spectrometer file reference number (FRN) document how and when the extract or sample was analysed and where the raw data is stored.

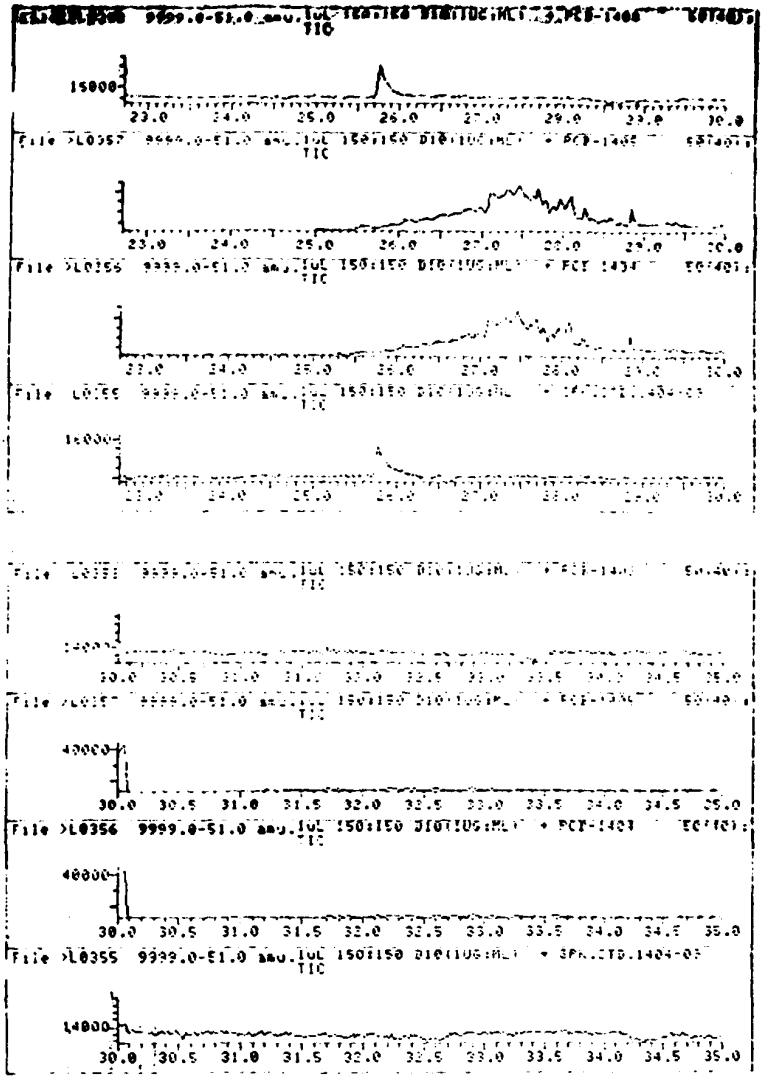
At the bottom of each table, analysts involved in extraction and analysis are listed, along with provisions for signature of the responsible analyst. This table format is both compact and precise. It was developed in an attempt to quickly and accurately generate data which the customer can quickly and accurately evaluate. It should include all required information for certification. If there are any suggestions concerning this format, please contact me at extensions 396, 209, or 409.

B. Mason Hughes
Senior Research Specialist

Environmental Sciences Center
Monsanto Company
Dayton Laboratory
1515 Nicholas Road
Dayton, Ohio 45407

File: 1MEXPT:MH:SP

The following pages show calculations or raw data documentation of reported results.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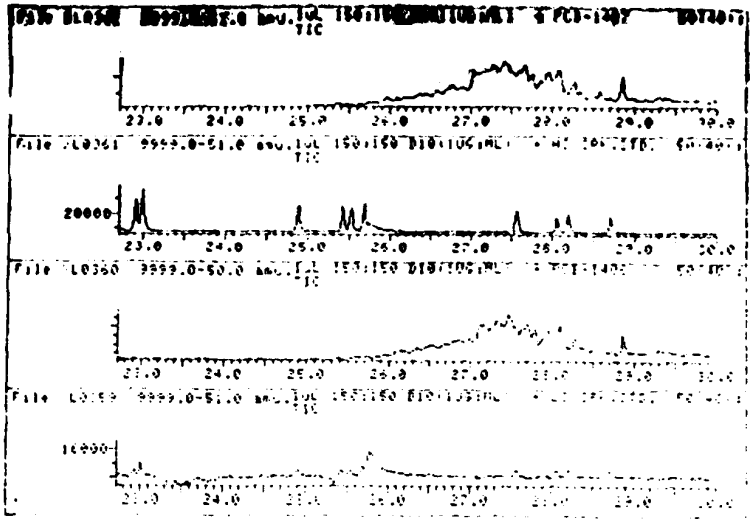
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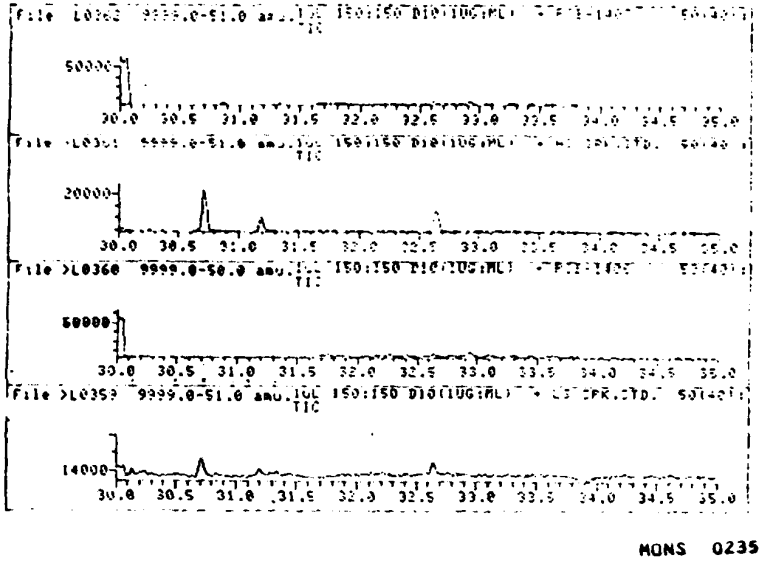
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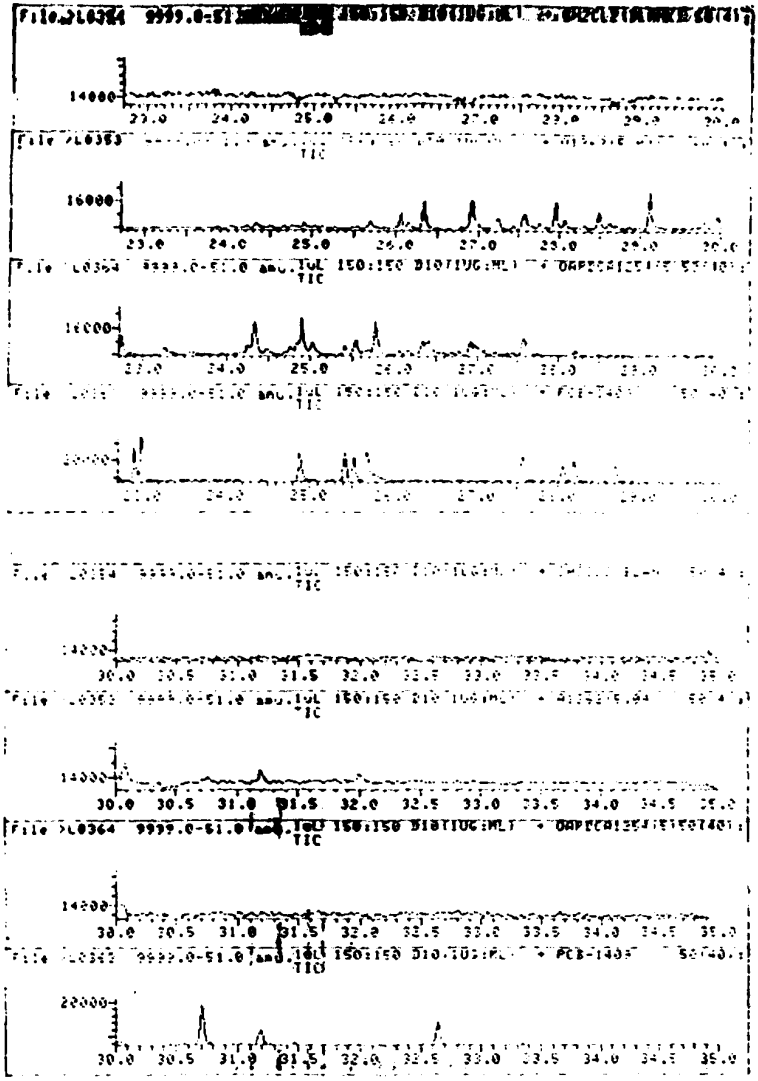
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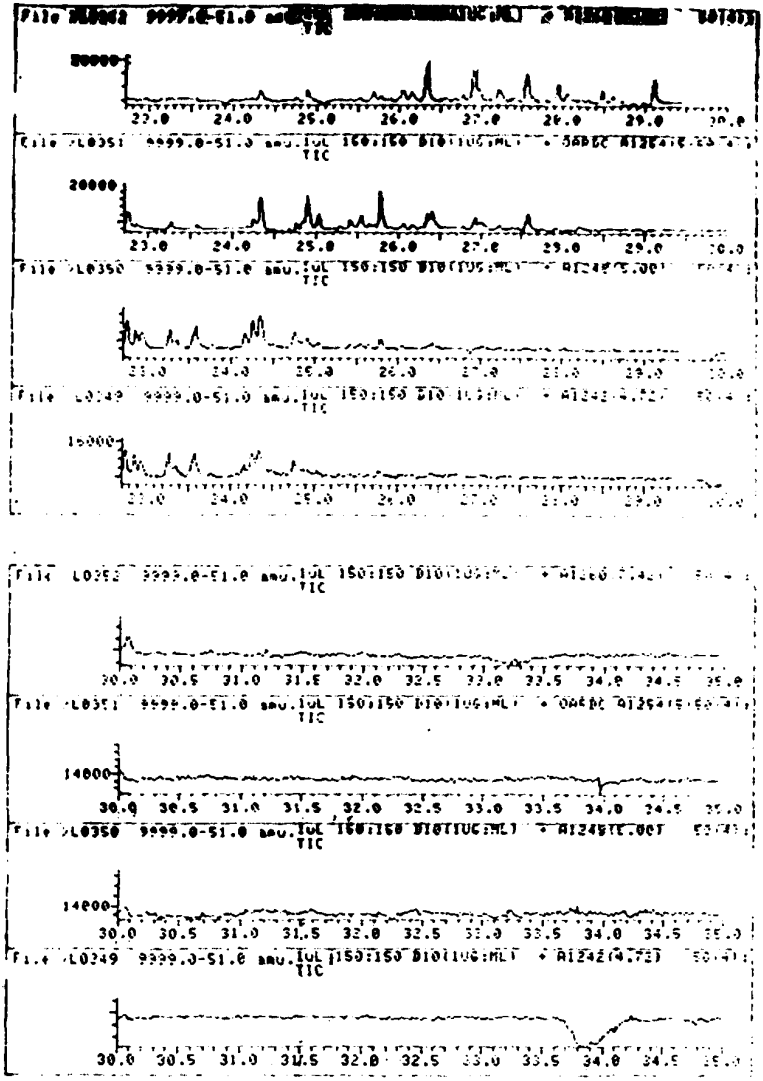
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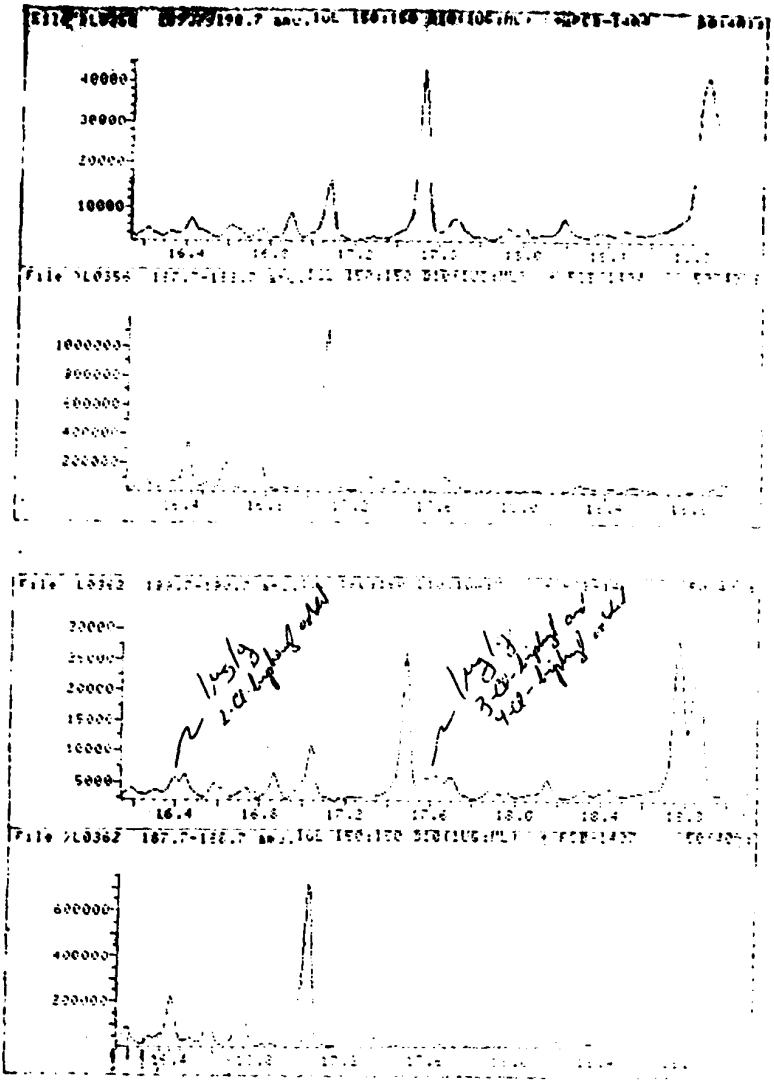
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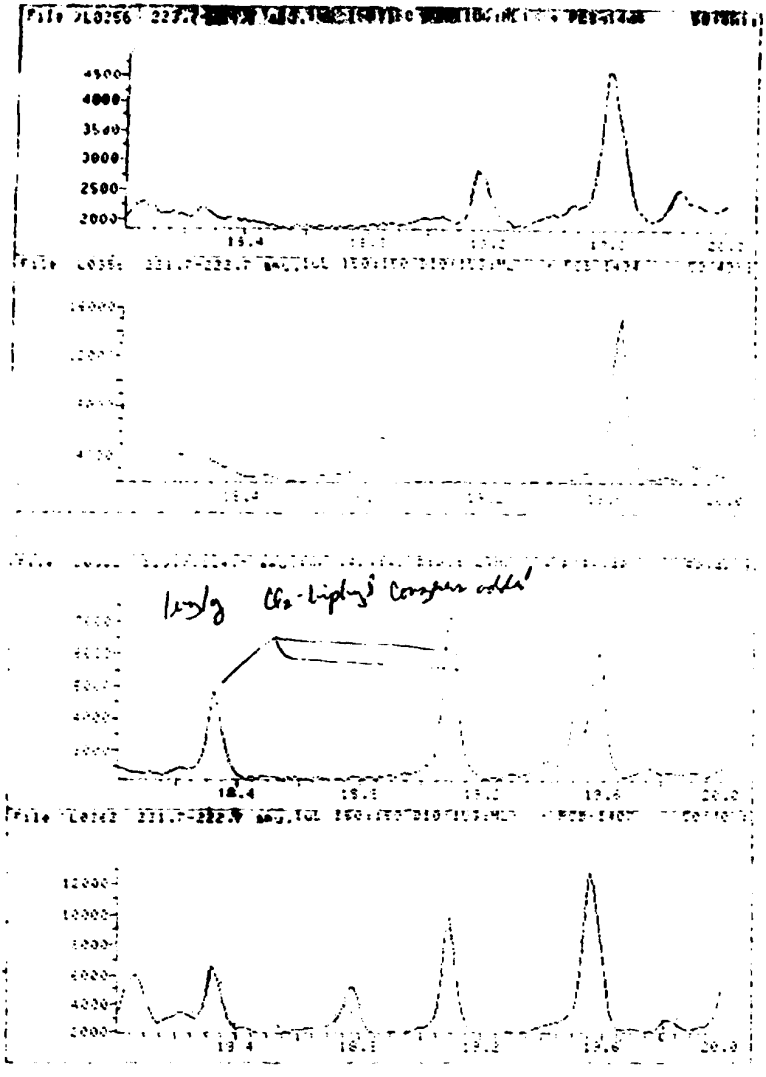
MONS 023574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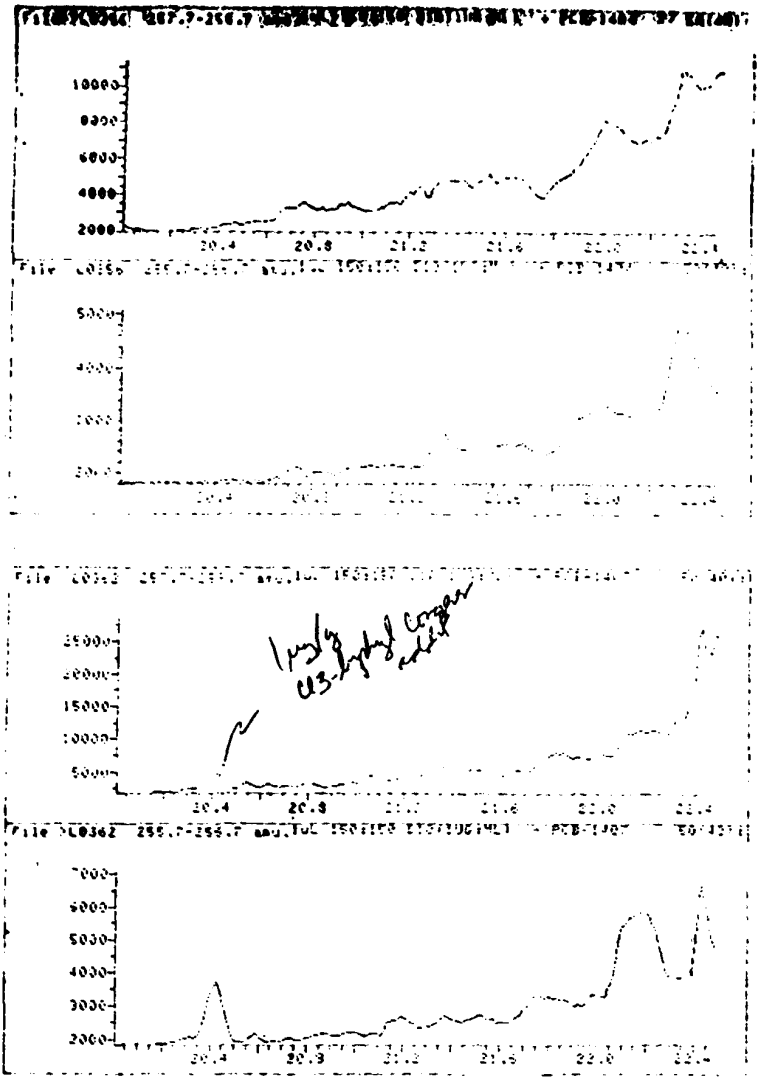
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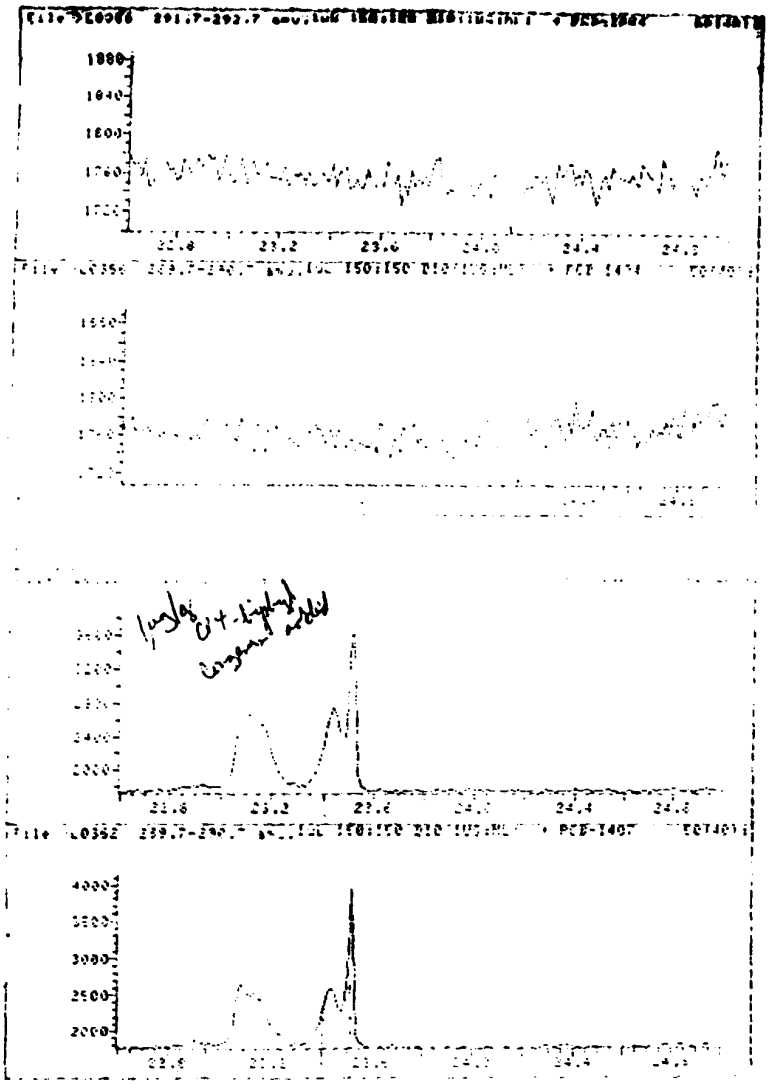
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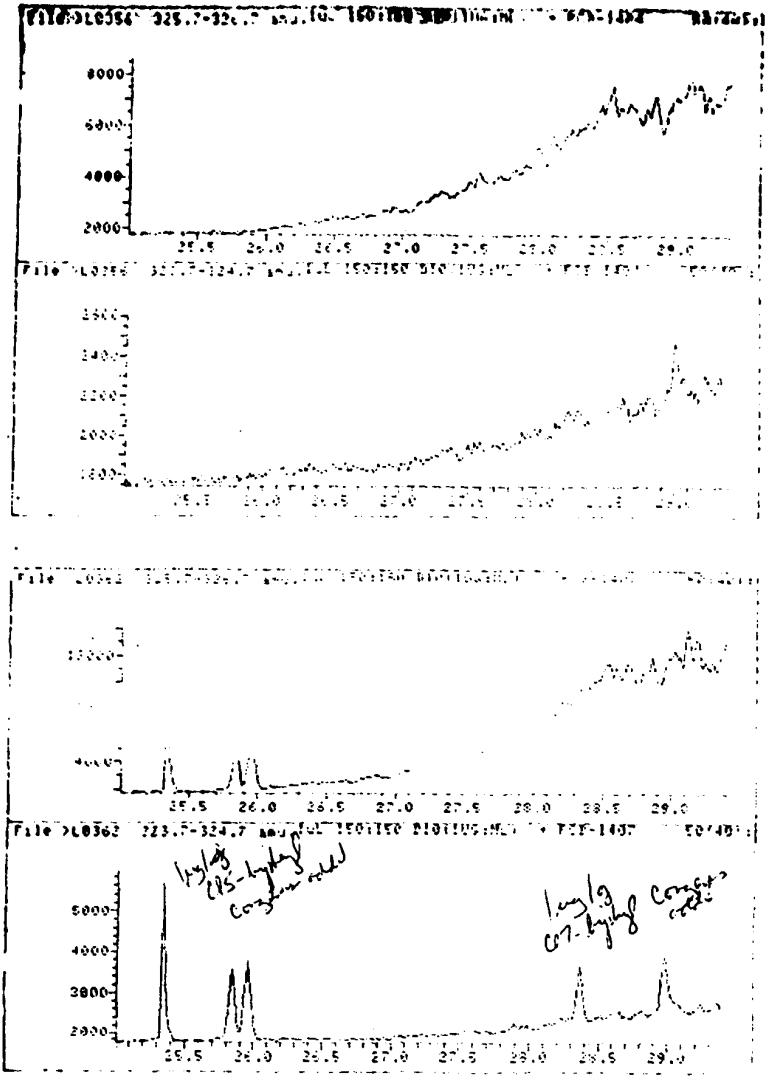
MONS 023577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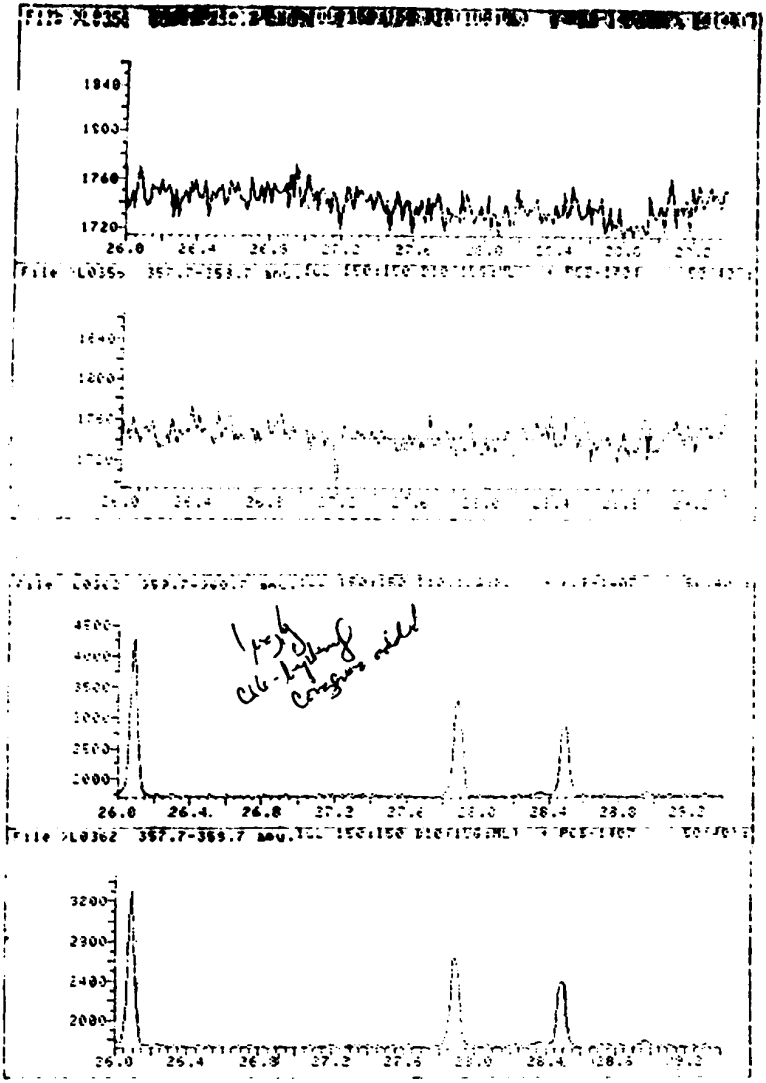
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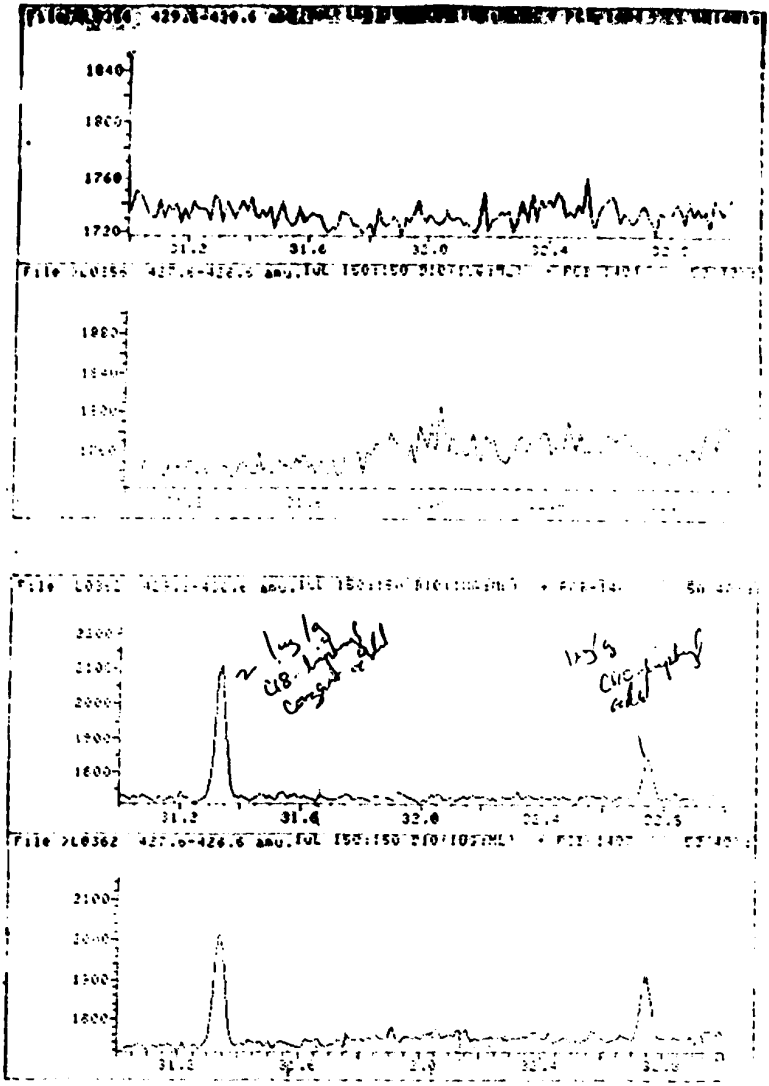
3000
2500
2000
1 µg/g
C16-hydroxy
coregrous oxide
File >L0362 357.7-359.7 amu.
3200
2800
2400
2000

MONS 023579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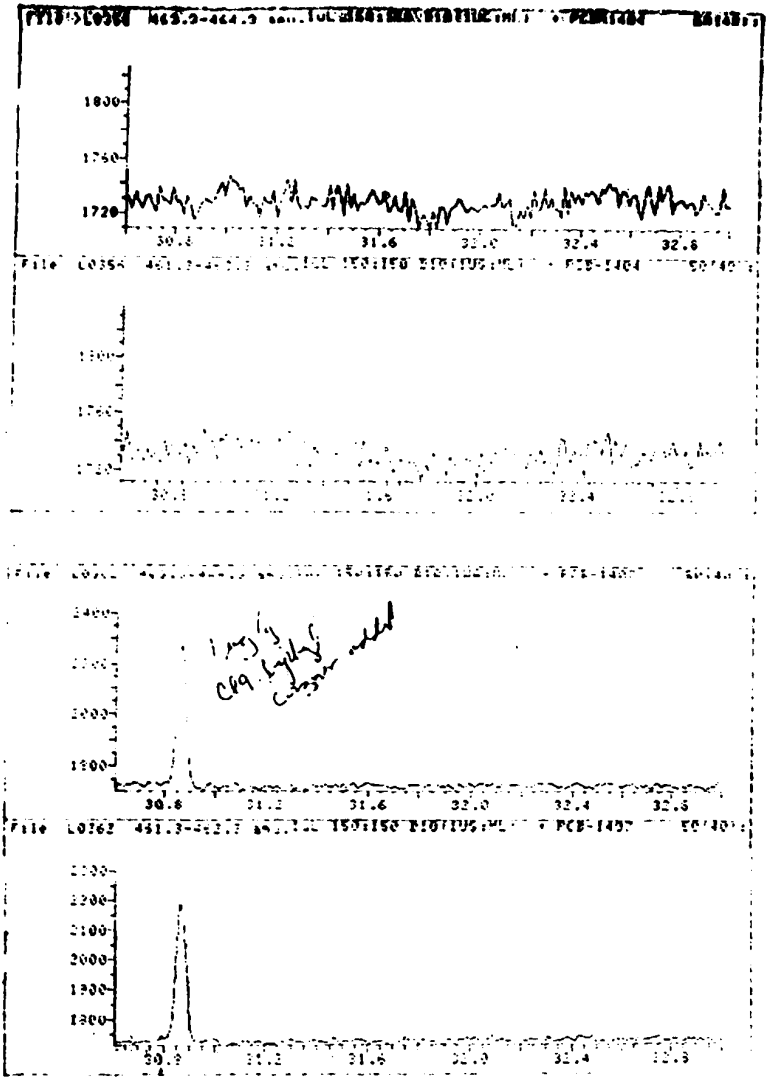
MONS 023580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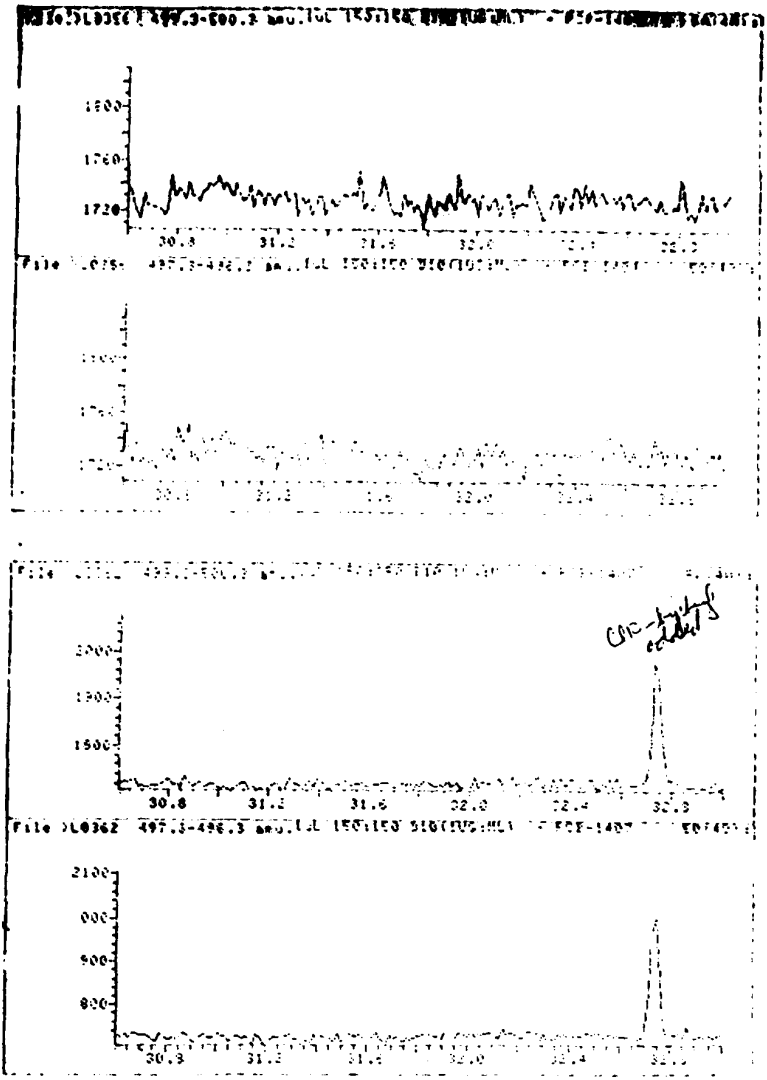
MONS 023581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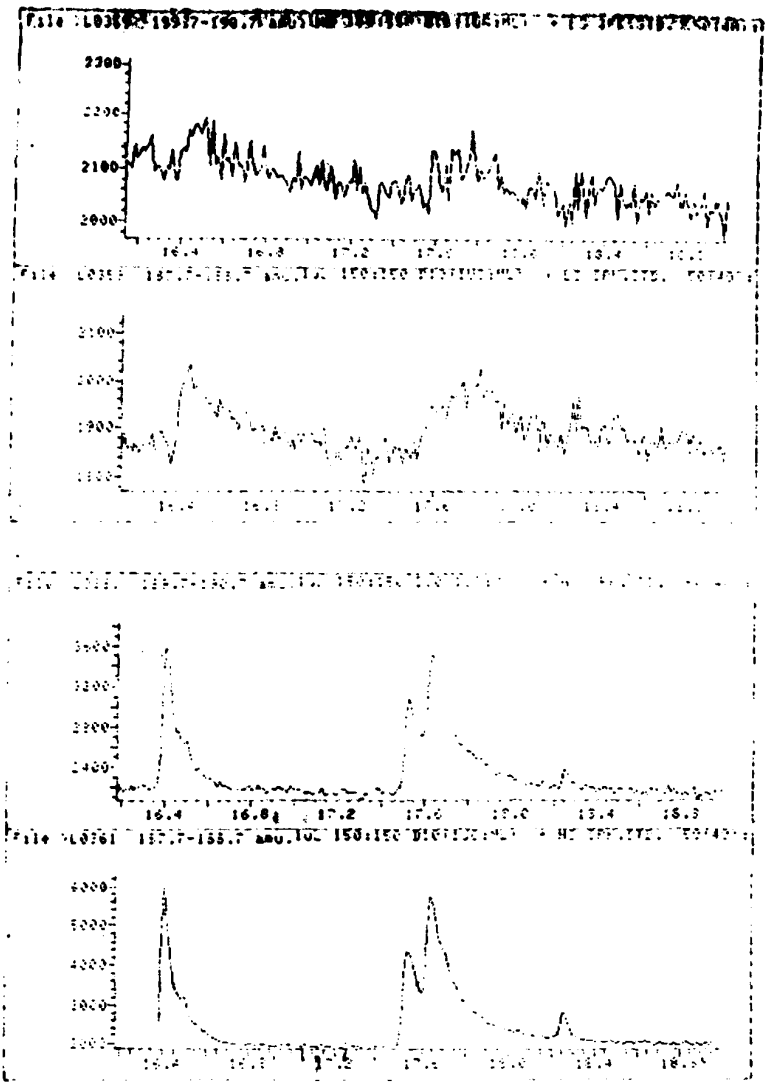

The following pages describe Standard Extraction Methods and Standard Analysis Methods used for this project.

ESC Standard Extraction Method (SEM)
TITLE: PCBs in Non-EC Active Matrices

ESC Standard Extraction Method No: PCE521

MATRIX,(CES):	TYPICAL SAMPLE SIZE (g)	TYPICAL EXTRACT VOLUME (ml)
Soils and other non-EC active solids and solvents	0.5 - 5.0	10

TYPICAL ANALYTES: Aroclors 1232, 1242, 1248, 1254, 1260, 1262, trichlorobiphenyl isomers through octachlorobiphenyl isomers

ESC Standard Analysis Method Nos: ECAM01, ECAM02

INTERFERENCES: Any electron capturing species in the retention time region of trichlorobiphenyl isomers through octachlorobiphenyl isomers that is non acid hydrolyzable

TYPICAL SURROGATES	TYPICAL RECOVERIES (%)
pentachlorobenzene	50 - 120
2,4,6-trichlorobiphenyl	50 - 120

APPARATUS AND MATERIALS:
Burdick and Jackson benzene or hexane for sample extraction or dilution.
Pierce vials.
Sulfuric acid at varying concentrations.
Ultrasonic bath.
Disposable glassware.
(See flow sheet for this extraction method in PCFS21.)

LIMITATIONS: Method applies only to matrices which do not contain interfering electron capturing species in the trichlorobiphenyl through octachlorobiphenyl isomer retention time region.

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

DATES OF METHOD CREATION AND UPDATES: 12/17/84

FLOW SHEET PCPS21

FOR ESC EXTRACTION METHOD PCEX21

SAMPLE ID: ---------- MRC EXTRACT # ----------

---------- LOG NO: ----------

EXTRACTION DATE and TIME: ----------

SAMPLE COLOR AND DESCRIPTION ----------

WEIGH OUT SAMPLE INTO A 14 OR 40 mL PIERCE VIAL	[ ]	SAMPLE WEIGHT----------
SURROGATE SPIKE OF SAMPLE	[ ]	----------

ADD 10.0 mL BENZENE TO SAMPLE.	[ ]	
ULTRASONICATE SAMPLE FOR 1/2 HOUR IN A SOUND BATH.	[ ]	
PLACE 2 mL OF THE EXTRACT INTO A 7 mL VIAL	[ ]	
ADD 2 mL ------ SULFURIC ACID AND SHAKE	[ ]	
ALLOW PHASES TO SEPARATE REMOVE 1 mL FOR ANALYSIS.	[ ]	FINAL VOLUME ---------- 10.0 mL

EXTRACT NO: ----------

DATE/TIME COMPLETED ----------

ANALYST: ----------

ESC JOB NO: ----------

MONS 023586

ESC Standard Extraction Method (SEM)
TITLE: PCBs in acid hydrolizable or ionizable matrices

ESC Standard Extraction Method No: PCEX14

MATRIX(X),(CES):	TYPICAL SAMPLE SIZE (g)	TYPICAL EXTRACT VOLUME (ml)
Chemical products which are acid hydrolizable or ionizable, ie. aniline and aniline derivatives and relatively pure basic compounds which exhibit a steichemetric end point.	0.5 - 1	1 - 10

TYPICAL ANALYTES:A1232,A1242,A1248,A1254,A1260 and A1262 and PCB isomers mono- through deca-chlorobiphenyl.

INTERFERENCES:	TYPICAL SURROGATES	TYPICAL RECOVERIES (%)
Any electron capturing species in the retention time region of monochlorobiphenyl isomers through decachlorobiphenyl isomers for ECANO1 and ECANO2. Any species in the appropriate retention time region which give the same relative characteristic mass responses as PCB isomers for MSANO3.	pentachlorobenzene	50 - 120
	2,4,6-trichloro-biphenyl	50 - 120
	3,3',4,4'-tetra-chlorobiphenyl-d6	50 - 120

APPARATUS AND MATERIALS:
Burdick and Jackson hexane for column elution and extraction solvent.
Sulfuric acid for ionizing and hydrolizing esters, ethers, bases, and alcohols.
Silica gel columns impregnated with potassium permanganate, sulfuric acid, and potassium hydroxide.
Disposable glassware.
(See flow sheet for this extraction method in PCFS14.)

LIMITATIONS: Method applies only to matrices which contain hydrolizable or ionizable electron capturing species in the monochlorobiphenyl through decachlorobiphenyl retention time region using EC detection methods.
PLEASE NOTE!! MS SAMS are valid only for PCB isomers from CL3-BP through CL10-BP due to reactivity of CL1-BP and CL2-BP to 80% sulfuric acid cleanup.

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

DATES OF METHOD CREATION AND UPDATES: 7/25/84

FLOW SHEET PCP814

FOR ESC EXTRACTION METHOD PCEX14

SAMPLE ID: ---------- NRC EXTRACT # ----------

---------- LOG NO: ----------

EXTRACTION DATE and TIME: ----------

WEIGH OUT SAMPLE INTO A 14
OR 40 mL VIAL [ ] WEIGHT SAMPLE (1 g) ----------

SURROGATE SPIKE OF SAMPLE [ ] SPIKE ----------

%

ADD ---- mL ---- SULFURIC [ ] RECORD AMOUNT SULFURIC ACID REQUIRED
ACID AND SHAKE TO SOLUBALIZE SAMPLE IN AQUEOUS MEDIA
NOTE - acid should be added
slowly or gradually [ ] RINSE COLUMN WITH 2 X 20 mL
to avoid violent HEXANE
reactions.

EXTRACT 3 X 4 mL WITH HEXANE [ ]

COLUMN DESCRIPTION
25 mL DISPO PIPET

1 cm Na SO
2 4

4 cm 1% POTASSIUM
PERMANGANATE
SILICA GEL

REDUCE SAMPLE VOLUME TO
3-4 mL WITH NITROGEN AND [ ]
APPLY TO COLUMN QUANTITATIVLY

1 cm SILICA GEL

ELUTE WITH 40 mL HEXANE [ ]

4 cm ACID SILICA
GEL

NITROGEN BLOW DOWN TO 1 mL [ ]

1 cm SILICA GEL

4 cm BASE SILICA
GEL

\XXX/ GLASS WOOL
\ /

EXTRACT NO:---------- ----------

DATE/TIME COMPLETED----------/----------

ANALYST:---------- ESC JOB NO:----------

MONS 023588

ESC Standard Analysis Method (SAM) — ESC Standard Analysis Method No:
TITLE: Aroclor Formulations in Solvents — ECAM02

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 RRF)(isomer area/internal standard area)

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.

DATE OF METHOD CREATION: 10/25/83, 2/3/84 Time Stamp - <850201.1123>

ESC Standard Analysis Method (SAM) — ESC Standard Analysis Method No:
TITLE: Organic Compounds in Solvents — MSAM03

ANALYTICAL INSTRUMENT AND MODE OF OPERATION: HP-5985/5987 Capillary GC/MS-Selected Ion Monitoring with RTE-VI operating system.

Typical Run Time:	3 - 40 min.
Typical Multiplier Voltage:	1800 - 2800 eV
Typical Dwell Times:	200 - 500 msec/mass
Maximum # of Masses:	20 masses x 5 ranges = 100 masses
Electron Energy:	70 eV

TYPICAL ANALYTE	TYPICAL INSTRUMENT LEVEL OF DETECTION (LOD) (ug/ml)	TYPICAL PRECISION @ 10X LOD (%)	TYPICAL ACCURACY @ 10X LOD (%)
Organic Compounds eluting between toluene and n-C34-ane	0.01 - 0.1	30	30

INTERFERENCES AND LIMITATIONS: Analyte characteristic mass must be chromatographically resolved from other eluting compounds which produce the same mass.

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

COLUMN TEMPERATURE PROGRAM: 50(4)/8/300 — INJECTION TYPE: Splitless

CALIBRATION AND STANDARDIZATION:

Quantitative: Use internal standard quantitation technique and calibrate instrument response factors from standard solutions of analytes of interest.

Qualitative: When multiple characteristic masses are monitored for a given analyte, the ratio of characteristic mass responses must be within 20% of those for the authentic standard. For PCB analyses, the characteristic masses which are monitored are the molecular ion containing all 35-CL isotopes and the molecular ion containing one 37-CL isotope. The following table summarizes the masses and approximate retention time regions monitored for the analysis of internal standard, surrogate standards, and chlorobiphenyl (CL-BP) through decachlorobiphenyl (CL10-BP) PCB congeners.

Analyte	Masses	Retention Times (minutes)	Relative Retention Times (a)
CL-BP isomers, anthracene-d10	188,190	16 - 22.5	0.60 - 0.84
CL2-BP isomers	222,224	16 - 22.5	0.60 - 0.84
Pentachlorobenzene surrogate	247.9,249.9	16 - 22.5	0.60 - 0.84
CL3-BP isomers	255.9,257.9	16 - 22.5	0.60 - 0.84
CL4-BP isomers	289.8,291.8	22.5 - 30	0.84 - 1.12
3,4,3',4'-CL4-BP-d6 surrogate	296,298	22.5 - 30	0.84 - 1.12
CL5-BP isomers	323.9,325.9	22.5 - 30	0.84 - 1.12
CL6-BP isomers	357.8,359.8	22.5 - 30	0.84 - 1.12
CL7-BP isomers (b)	323.9,325.9	22.5 - 30	0.84 - 1.12
	391.8,393.8	30 - 50	1.12 - 1.87
CL8-BP isomers	427.7,429.7	30 - 50	1.12 - 1.87
CL9-BP isomers	461.6,463.6	30 - 50	1.12 - 1.87
CL10-BP	497.6,499.6	30 - 50	1.12 - 1.87

(a) Relative Retention Times calculated using a retention time of 26.78 minutes for 3,4,3',4'-CL4-BP-d6.
(b) CL7-BP isomers are analyzed using either CL2-loss characteristic ions (m/e 323.9 and 325.9) or molecular ions (m/e 391.8 and 393.8).

CALCULATIONS: Analyte concentration = (Analyte area)/[(Analyte RRF)(IS area)]

where: Analyte area is the characteristic mass area of the analyte.
RRF is the relative response factor for the analyte.
IS is the internal standard and is usually anthracene-d10.

RRF = (analyte area in standard)/[(analyte conc.)(IS area)]

PCB concentrations are calculated in one of two ways:

1) If an Aroclor formulation can be identified from the patterns of PCB isomers, selected PCB isomers or classes of isomers (i. e. all CL4-biphenyl isomers) are used to quantify the Aroclor concentration. Relative Response Factors are calculated using the concentration of the total Aroclor formulation in the above RRF equation.

2) If no unique Aroclor formulation is present, then the total PCB concentration is calculated by using standard solutions containing known amounts of chlorobiphenyl through decachlorobiphenyl isomers to calculate Relative Response Factors for each chlorine class in the above RRF equation. The RRFs for the corresponding PCB isomer classes are used to calculate total PCB isomer concentrations of each class in unknown samples.

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

DATE OF METHOD CREATION: 12/9/83 Time Stamp - <850719.0936>

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

Time Stamp = (850730.0949)

MONSANTO COMPANY/DAYTON LABORATORY

ENVIRONMENTAL SCIENCES CENTER

ANALYSIS REQUEST

DATE: 7-11-85 LOG NO: 1-85-07-11-01

REQUESTER: NIC/IVORY PROJECT NO: 760.18 - 327

REPORT RESULTS TO: FILES/MEES, IVORY, SHERMAN, HUGHES, HILEMAN, McKENZIE

ANALYSIS REQUESTS SENT TO: FILES, IVORY, SHERMAN, HUGHES, HILEMAN,McKENZIE

SAMPLE PICKUP BY: HILEMAN

SAMPLE LOCATION: LAB 28 BUILDING 2

SAMPLE DESCRIPTION FOR 6 SAMPLES

SAMPLE IDENTIFICATION	NUMBER OF BOTTLES	ESC NUMBER(S)
Q1042-1, RO-01-00	1 qt.	PCB-1404,PCB1405-DUP PCB-1406-LS,PCB-1407-HS
METHOD BLANK		PCB-1408
METHOD BLANK + HS		PCB-1409
Q1042-1, GS-01-00	2 X 40 mL	PCB-1399, PCB-1400-DUP
Q1042-1, GS-01-01	100 g	PCB-1394, PCB-1395-DUP
Q1042-1, GS-02-01	100 g	PCB-1396
Q1042-1, GS-03-01	100 g	PCB-1397
Q1042-1, GS-04-01	100 g	PCB-1398
BLANK DAYTON SOIL		PCB-1401
BLANK DAYTON SOIL + LS		PCB-1402
BLANK DAYTON SOIL + HS		PCB-1403

RECORDED BY: McKENZIE

REQUIRED ANALYSES: DIOXIN(S) AND PCB(S)

ANALYTICAL TECHNIQUES:

TECHNIQUE (EN)	DATE COMPLETED	TECHNIQUE(EN)	DATE COMPLETED
x GC/EC (1B)	7/30/85	x GC/MS (1B)	7/30/85

QUALITATIVE: SEMIQUANTITATIVE: QUANTITATIVE: X

REQUIRED QA/QC: SEE GOOD LABORATORY PRACTICES MANUAL

COMPLETION DATE REQUESTED: ASAP

COMMENTS:

SAMPLE DISPOSITION: -- - HOLD FOR 60 DAYS

SAFETY PRECAUTIONS: SEE SAFE LABORATORY PRACTICES MANUAL

ANALYSIS REQUEST FILE NAME: AB327:LI

The following is a copy of the ESC/EBC Good Laboratory Practices Manual.

Copy Numbers _____

GOOD LABORATORY PRACTICES MANUAL

A Guide to Quality Control/Quality Assurance

Ultratrace Analysis Group

March 1984

Joseph J. Brooks
Joseph J. Brooks
Group Leader, Ultratrace Analysis

H. A. Wollermann
Manager, Environmental Sciences Center

Issued to: _____

Date: _____

Environmental Sciences Center
Dayton Laboratory
Dayton, Ohio 45407

JBJ/JOB A

MONS 023595

TABLE OF CONTENTS

		Page
I	Objectives	1
II	Scope	1
III	Analysis	1
	A. Methods	1
	B. QA/QC Program	2
	1. Sample Preparation QA/QC	2
	a. Method Blanks	2
	b. Replicates	2
	c. Spikes	2
	2. Instrumental Analysis QA/QC	3
	a. Instrumentation	3
	b. Blanks	4
	c. Quantitation Internal Standard	4
	d. Standards	4
	C. Degrees of Quantitation	4
	1. Qualitative Analysis	7
	a. Tentative	7
	b. Confirmed	7
	2. Semi-Quantitative Analysis	7
	3. Quantitative Analysis	7
	D. Quality Criteria and Remedial Action	8
	1. Quality Criteria	8
	a. Blanks	8
	b. Recoveries	8
	c. Precision	8
	d. Limit of Detection	9
	e. Accuracy	9
	2. Remedial Action	9
IV	Data	9
V	Sample Disposal	10

FIGURES

Figure		Page
1	Example of GC/MS Logbook page	5
2	Example of GC/EC Logbook page	6
3	Example of Disc/Tape Logbook page	11

I. Objectives

The main objectives of the Ultratrace Analysis Group quality assurance/quality control program are: 1) to assure that our laboratory generates high quality results; and 2) to maintain the necessary records that document laboratory performance.

II. Scope

The scope of this manual includes areas of GLP not specifically addressed in the ESC section manual and expands upon certain areas where QA/QC practices differ from those described in the section manual. It is intended to be used along with the section manual to provide a complete picture of the GLP within the Ultratrace Analysis Group.

III. Analysis

The generation of analytical results within the Ultratrace Analysis Group routinely involves two processes: sample preparation and instrumental analysis. Sample preparation involves one or more of a variety of techniques including extraction, dilution, acid/base washes, column chromatography, concentration and numerous other techniques to render the sample in a suitable condition for instrumental analysis. Instrumental analysis takes the suitably prepared sample and introduces it into an analytical instrument to measure the desired parameter(s). Both of these processes can be described by clearly defined and separable methods called sample preparation methods (SPMs) and instrumental analysis methods (IAMs). SPMs and IAMs may be combined in numerous ways (depending upon the nature of the samples and the needs of the customer) to produce a successful analytical protocol. For example, several different SPMs may be used to produce samples that are suitable for analysis by a single IAM. The measures incorporated into each of these experimental processes to ensure that an assessment of the quality of the results can be made constitute the QA/QC program for a project. The following subsections describe the elements of the analysis process:

A. Methods

Methods are the written documentation that describe the analytical process. They contain sufficient detail such that a competent scientist or technician can readily perform the required analyses. The usual practice is to have methods that describe the sample preparation process (SPMs) and methods that describe the instrumental analysis process (IAMs). Each method developed within the Ultratrace Analysis Groups is assigned a method number as described in the ESC Section Manual.

Methods are obtained from various sources including in-house development, modification/adaptation of literature methods, or specific protocol methods dictated by government agencies. Methods may be formally validated by a series of experiments that describe a classical validation protocol or may be less vigorously proven owing to factors such as frequency or use, customer needs and

MONS 023597

cost/timing restrictions. In any case a QA/QC program is applied to the analysis process to provide a measure of the quality of the results. Unless a QA/QC program is prescribed by a required protocol (e.g., EPA Dioxin in Soil protocol), certain minimum QA/QC measures (depending upon the analysis type) are incorporated into all Ultratrace Analysis projects. The following subsection describes the Ultratrace QA/QC program:

B. QA/QC Program

An effective QA/QC program incorporates experiments that provide information relative to each of the following questions:

(1) Are there any impurities, background or contamination that will influence the results?

(2) How reproducible are the results?

(3) How well can the analyte be recovered from the sample matrix?

(4) What is the limit of detection for the analysis?

(5) What is the dynamic range of the analysis?

(6) What is the accuracy of the analysis?

All of these questions are addressed by properly selecting/applying the use of blanks, replicates, spikes and standards in a QA/QC program. The discussion of the use of these QA/QC techniques as they apply to Ultratrace Analysis Group activities is best done by considering the sample preparation and instrumental analysis processes separately.

1. Sample Preparation QA/QC

   a. Method blanks - Representative glassware, solvents and reagents are used with sample matrices which are similar to those for which results are being reported, yet do not contain the analytes of interest. Method blanks are analyzed at a frequency equal to 10% of the analyzed samples for sample sets which are multiples of 10. At least one method blank is analyzed for sample sets containing between 1 and 9 samples.

   b. Replicates - If sufficient sample amounts have been submitted for analysis, replicate frequency is the same as the method blank frequency. If at all possible, replicates should be obtained from the same sample bottle in order to minimize sample inhomogeneity problems due to samples being taken at slightly different times.

   c. Spikes - If sufficient sample is available for each sample type, the sample is split and spiked at two levels with

MONS 023598

the native (unlabeled) analyte(s). The levels are typically 2x (low) and 20x (high) the anticipated detection limit and serve as a technique for estimating the limit of detection for each matrix. These low and high spikes are conducted at a frequency equal to the Method Blank frequency. Obviously spiking with the native analyte cannot be done for widescan analysis since this presupposes knowledge of the identity of the analyte(s) in the sample.

Other spiking techniques are used to evaluate the extraction/recovery efficiencies for the analyte(s) of interest. Ideally extraction/recovery efficiencies are determined for each sample, since, in principle, each sample may represent a different matrix. This can be done very easily when the detection technique is mass spectrometry if an isotopically labeled version of the analyte(s) is available. Documentation of extraction/recovery efficiencies is not required for each sample if the sample matrix for a set of samples is constant. However, for a sample set for which the similarity of samples is not known, and for which adequate sample is available, each sample must be split and spiked with a known amount of the analyte(s) of interest to determine extraction efficiency. If adequate sample size is not available or the identity of the analyte(s) is not known before the fact (i.e., widescan analysis), surrogate spiking compounds may be used to assess extraction efficiencies in each sample without actually spiking each sample with the analyte(s) of interest. The choice of the surrogate spiking compound is tailored for each analyte. This surrogate must be chosen so that it is either chemically identical to the analyte of interest (for example using isotopically labeled analogues of the analytes), or is closely similar in terms of liquid/liquid partition properties, chemical reaction properties, column elution properties or other matrix isolation properties which are used to isolate the analyte(s) from the sample matrix. Another property of the surrogate spiking compound is that it not be present in the sample being analyzed.

2. Instrumental Analysis QA/QC

The final step in obtaining analytical results involves the use of an appropriate instrumental technique to produce the analytical data. Several QA/QC practices must be incorporated in this process to ensure validity of the data.

a. Instrumentation

Careful documentation of instrument usage, calibration, and maintenance is essential for the generation of high quality results. Each major instrument within the Ultratrace Analysis Group will be the assigned responsibility of a professional employee designated as the Instrument Steward. The Instrument Steward is responsible for making sure that logbooks are available and properly completed by instrument users. It is the

MONS 023599

responsibility of each individual using the equipment to record all the pertinent data required in the logbook. An example of a page from a GC/MS logbook is given in Figure 1 and that of a GC/EC logbook is given in Figure 2.

Instruments will be calibrated according to the instrument manufacturers' specifications or according to the method being used with the instrument. A log of instrument calibration will be maintained with the instrument.

The Instrument Steward will be responsible for ensuring that preventative and corrective maintenance programs are carried out on all instruments under his/her responsibility. If a specific problem is noted by an instrument user, it should be noted in the logbook and the Instrument Steward notified so that appropriate corrective action can be taken.

b. Blanks

A solvent blank will be analyzed at a frequency equal to the method blank. The method blank can serve as the solvent blank provided it is clean in the area of the analyte(s) of interest. This practice eliminates the possibility of background instrumental contamination.

c. Quantitation Internal Standard

A quantitation internal standard will be added to each sample following sample preparation but prior to instrumental analysis. This compound will serve for determining relative response factors and for correcting for variations in sample injection volumes and evaporation of solvents.

d. Standards

Standards are solutions of the analyte(s) of interest used to determine the response of the detector over the range of analyte concentrations found in the samples. For Quantitative analyses, sufficient standards and replication of standards will be run to demonstrate linearity and precision of the detector response over the range of analyte concentrations. Should sample concentrations fall outside the demonstrated linear range, either additional standards are prepared to expand the range, or appropriate dilution/concentration of the sample is done to place it in the proper range.

C. Degrees of Quantitation

The information provided for any particular analysis is tailored to the needs of the customer. In actual practice these needs vary across the broad continuum from the grossly qualitative to the precisely quantitative. It is informative to examine what is involved in providing the varying degrees of quantitation required by our customers.

HP 5985A

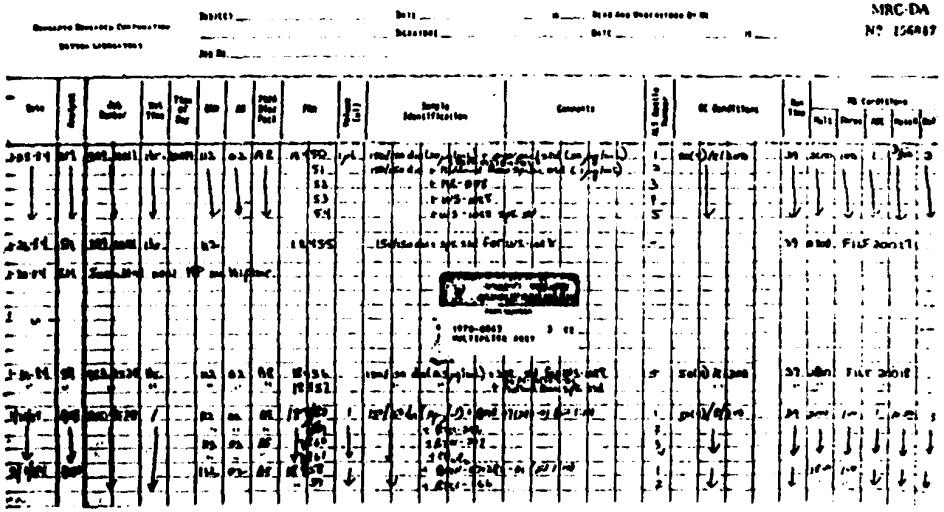

FIGURE 1. Example of GC/MS Logbook page.

HP 5880 QC/EC

MRC-DA
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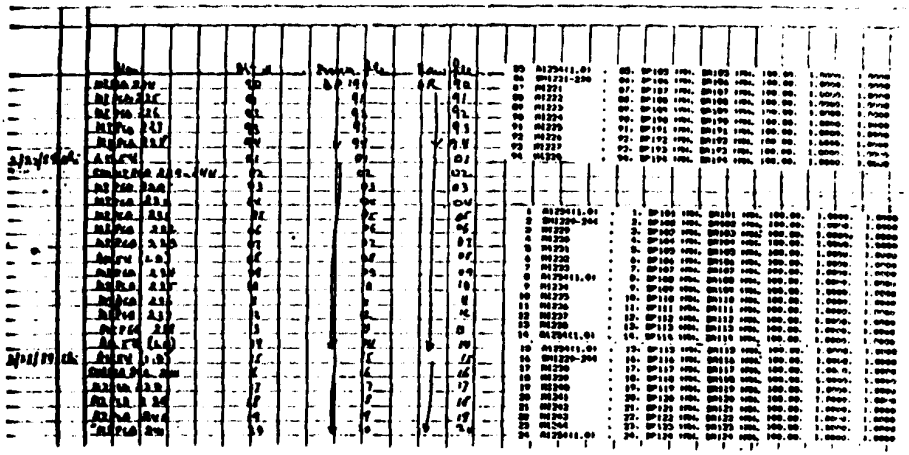

FIGURE 2. Example of CC/EC Logbook page.

MONS 023602

1. Qualitative Analysis

Qualitative analysis implies no quantitation at all but rather seeks only the identity of the compound(s) present. GC/MS is particularly applicable to this type of analysis problem. Two types of identifications can be made:

a. Tentative

A tentative identification is made on the basis of the analyst's judgement of a match between the mass spectrum from the sample and a mass spectrum from a reference library. This is often done for the large number of compounds found in a widescan organic analysis.

b. Confirmed

A confirmed identification requires that the chromatographic retention time and the mass spectrum of the unknown compound match those of a known standard of the tentatively identified compound. This is often done in widescan analyses when standards can be obtained for tentatively identified compounds that are of concern.

The normal QA/QC requirements for qualitative analysis are (1) analysis of a blank, (2) analysis of duplicate samples and (3) use of a calibration compound (usually Decafluorotriphenylphosphine, DFTPP) to assure that the mass spectrometer will produce mass spectra that can be compared with library spectra.

2. Semi-Quantitative Analysis

Semi-Quantitative Analysis extends the information provided by a qualitative analysis to include some estimate of the amount of analyte(s) present. The method of semi-quantitation involves the comparison of detector response of the analyte(s) with that of an internal standard. The estimated concentration is obtained by assuming a unit response factor between the analyte(s) and the internal standard(s). An indication of recovery from the sample matrix is obtained from the recovery of the surrogate internal standard(s).

3. Quantitative Analysis

Quantitative Analysis provides for the accurate assessment of the amount of analyte(s) present in a sample. To be able to do quantitative analysis one must know the identity of the analyte so that standards can be prepared for spiking and for the generation of calibration curves. The method of quantitation is based on a three-point calibration curve using standards of the analyte(s) of interest over the range of concentrations in the samples. A one-point calibration method can be used (as with the laboratory data

MONS 023603

system) provided that linearity has been demonstrated over the concentration range of the samples using standards of the analyte(s) at three concentrations in the range. This calibration curve is then used to provide concentrations of the analyte(s) in the samples via an external standards method or more preferably via an internal standards method. For the internal standards method, the quantitation internal standard is added to each of the standards (just as with the samples) prior to instrumental analysis and relative response factors are determined.

For quantitative analysis the mass spectrometer is operated as a gas chromatographic detector. The MS is therefore tuned and operated in a manner specified in the approved method rather than using a calibration compound as required for qualitative analyses.

D. Quality Criteria and Remedial Action

The inclusion of QA/QC measures into an analysis program has little meaning unless the results are interpreted and appropriate action is taken when necessary. The ability to do this assumes some set of criteria that will trigger a response or remedial action. The following subsections describe the criteria that are used in the Ultratrace Analysis Group to evaluate when quality control data indicate a need for corrective measures and what remedial action will be taken.

1. Quality Criteria

The overriding quality criterion above all others is: Do the results meet the needs of the customer. This determination will be made jointly between the customer and the analyst. The analyst must exercise caution in not allowing the customer to overstate, misinterpret or unintentionally misrepresent the data. In addition to this prime quality criterion, the following conditions must be met:

a. Blanks - In the event that a blank produces a positive value, it may not be used as a valid blank if it exceeds 10% of any reported value for a sample.

b. Recoveries - Recoveries for all surrogate and native spikes must lie in the range of 50%<Recovery<150%.

c. Precision - Precision will be calculated based on the recoveries of surrogate internal standards. Average recoveries will be calculated with ± standard deviation for each sample set. Replicate analyses and low and high native spike recoveries may also be used to provide additional information/insight into the precision of the analysis.

d. Limit of Detection - The limit of detection (LOD) will normally be stated as ½ the value of the low level native spike if it is recovered and quantifiable. Should the low level native spike not be recovered, the LOD will be stated as ½ the value of the high level native spike if it is recovered and quantifiable. Should neither spike be recovered, a decision must be made regarding the advisability of reprocessing the sample. Should all samples contain such large quantities of the analyte(s) that the levels of the low and high spikes are insignificant (≤10%) by comparison, the value of the LOD becomes less important and is simply stated as the LOD for the instrumental analysis process determined by the analysis of standards and the ability to recover the surrogate spikes.

e. Accuracy - The accuracy of the analyses is best determined by analyzing some sample which contains the analyte at some predetermined level (e.g., an NBS standardized sample). If this type of standard is not available then the low level and high level spikes can be used as a measure of the accuracy of the analyses. Results must fall within a range of 75% to 120% of the excepted value for the analyses to be considered valid.

If the above quality criteria are not met the analyst will immediately assess the need for and extent of remedial action that may be necessary.

2. Remedial Action

The first course of action will be for the analyst and/or group leader to contact the customer and discuss the results pointing out the limitations of the data indicated by the quality control results. At this point the overriding quality criterion of customer needs will be addressed first. It could be that the customer's needs are met without meeting one or more of the other criteria. In such a case no remedial action is necessary. It could also be that the customer has such a demand for tightness in the results that his needs are not met even though the other quality criteria are. This would trigger further analyses with tighter quality control designed around the results obtained (e.g., replications of positives to better establish precision or spikes of non-detected samples to better establish the limit of detection).

In consultation with the customer additional experiments will be designed including the appropriate quality control to ultimately provide the results of sufficient quality to meet the customer's needs.

IV. Data

This section deals with the subject of data and how they are obtained, recorded and reduced so as to be useable in a report and yet readily available for referral and inspection.

MONS 023605

The samples will be labeled with a log number at sample login according to the procedure described in the ESC Section GLP Manual. When delivered to the responsible technical person, the samples may then receive additional labeling as deemed necessary. This additional labeling will be documented in a laboratory logbook and/or notebook. These logbooks and notebooks will be used by the analysts to record all pertinent work and results obtained from the samples. The laboratory notebooks will be filled out in accordance with Monsanto Uniform Notebook Procedures.

All raw data generated for a given project, which cannot be conveniently placed in the laboratory notebook (e.g., chromatograms, computer output, etc.), will be filed under some prescribed order (i.e., log number) in a central file under the supervison of the Project Leader and/or QA Specialist.

Most of the data generated by the Ultratrace Analysis Group are computer data stored on magnetic discs. In order to archive these data the specific file name and disc number associated with the analysis will be written down in the laboratory notebook and/or instrument logbook. When the disc is completely full of data an entire unedited disc image or copy of the files on the disc will be transferred to magnetic tape. A logbook will be kept for recording the disc number, name and prefix associated with it, along with the associated tape and file number to which the disc was transferred. An example of such a logbook is given in Figure 3. When the data are transferred a verification program is used to check all transferred records for correctness. When tapes are filled (they typically hold seven to ten disc images) they should be stored in a fireproof vault.

All calculations of the results of the data will be specified in the method used. These calculations will be entered in the analysts laboratory notebook unless they are computer generated. In this case, a copy of the computer output will be filed with the raw data. The Project Leader will be responsible for checking the correctness of the data.

V. Sample Disposal

Samples will be disposed of in accordance with the instructions on the Analysis Request form. The only exception to this would result when the analysis reveals a problem which requires sample disposal in a manner other than that originally specified. If the Project Leader notes from the results of the analysis that a potentially toxic product was present in the samples then the samples will be disposed of in a manner deemed safe by the Safety Department. The date of sample disposal and the manner should be noted on the request form stored with the raw data completing the chain of custody of the sample.

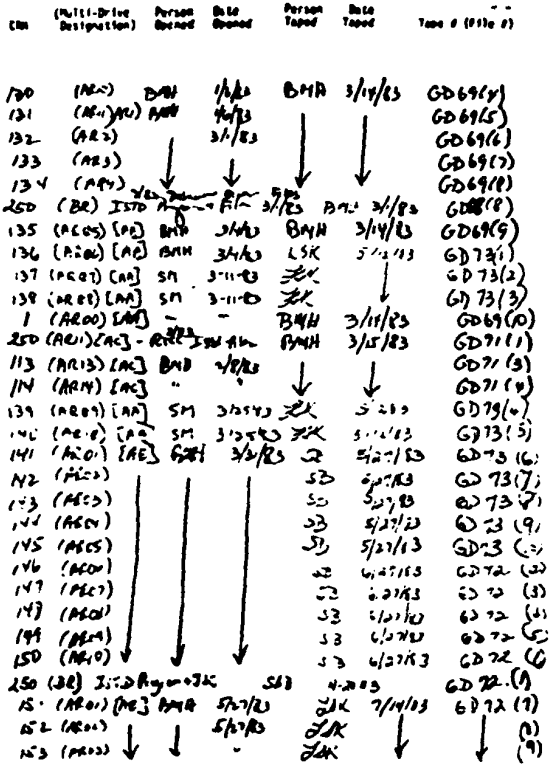

FIGURE 3. Example of DISC/Tape Logbook page.

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