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TITLE: ANALYSIS OF TETRATHAL FOR PCB'S AND PCDD'S

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

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ABSTRACT: A sample of Tetrathal was analyzed for possible PCB and PCDD concentrations. The results of these analyses are shown in this report.

TECHNICAL APPROVAL: J. J. Brooks
Senior Research Group Leader

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

APPROVAL DATE: 6-22-84

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MONS 220769

AUTHORS: F. Hileman and B. M. Hughes
TITLE: ANALYSIS OF TETRATHAL FOR PCB'S & PCDD'S
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ACKNOWLEDGEMENT

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

Analyses: F. Hileman
B. M. Hughes
D. McKenzie
J. Wendling

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ANALYSIS REPORT

DATE: June 20, 1984

LOG NUMBER: 1-84-02-08-02 PROJECT NO: 484.40718

TO:
Ivory/Pysz, St. Louis

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

Phone No: (513) 268-3411

Title: Incidental PCB Analysis for Tetrathal R TCPA 831.04

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

Standard Extraction Method No(s): PCEX07

Standard Analysis Method No(s): MSAN03

Final Report File No(s): A40718

Table File No(s): B40718

Table 1 summarizes incidental PCB results. Additional information is also provided concerning extraction and analysis methods used. A detailed description of the Incidental PCB Regulation and the ESC Good Laboratory Practices Manual is also included for your information.

As shown in Table 1, no incidental PCBs were detected above the LOQ listed for CL1-BP through CL9-BP. However two mass spectrometric responses were detected which could be attributed to a CL8-BP and a CL9-BP isomer at approximately 0.1 and 0.2 ug/g, respectively. These concentrations are well below the level of quantitation for these two compounds and could not be confirmed mass spectrometrically. The two values of 1.2 and 1.4 ug/g for CL10-BP are below the 2 ug/g LOQ required for reporting Incidental PCB generation as discussed in the Federal Register. However it is very important that several representative samples of tetrathal be analyzed in order to determine this value more accurately and also to determine what range of values are detected in tetrathals from various manufacturing lots.

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The tetrathal sample extracts shown in Table I were also analyzed using GSC/MS techniques while scanning over a mass range of 30 to 550 amu. This was done in order to confirm that the CL10-BP response is indeed due to this chlorinated biphenyl and to eliminate one response which appears to be due to hexachlorobenzene, rather than a PCB isomer. These analyses showed that hexachlorobenzene is present at concentrations greater than 1000 ug/g and that pentachlorobenzene is present at approximately 10 ug/g. The presence of these compounds, coupled with the possibility of pentachlorophenyl radical recombination in the production of tetrathal, may be the source of the CL10-BP PCB isomer detected in these samples. The concentration of the CL10-BP isomer was below the detection limit to obtain a complete mass spectrum of this component, however the retention time and responses for masses 427.7, 429.7, 497.6, and 499.6 are identical to the CL10-BP isomer in an authentic standard.

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

ANALYST APPROVAL: B. Mason Hughes

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Table 1. Results of Incidental PCB Analyses.

Project No: 484.40718 Date: June 28, 1984

			Sample Identification		
			Tetrathel B TCP 831.04	Tetrathal B TCP 831.04 (dup)	Method Blank
Congener Class	Analytical Method	LOQ(a) (ug/g)	Concentration (ug/g)		
CL1-BP	MSAN03	1(N)	NQ(b)	NQ	NQ
CL2-BP	"	"	"	"	"
CL3-BP	"	"	"	"	"
CL4-BP	"	"	"	"	"
CL5-BP	"	"	"	"	"
CL6-BP	"	"	"	"	"
CL7-BP	"	"	"	"	"
CL8-BP	"	"	"	"	"
CL9-BP	"	"	"	"	"
CL10-BP	"	"	1.2	1.4	"
Surrogate Spiking Compound		Amount Added(ug/g)	Recovery (%)		
3,4,3'4'-CL4-d6		1.0	102	131	95
Documentation					
ESC Extraction Method			PCEX07	PCEX07	PCEX07
Date of Extraction			6/19/84	6/19/84	6/19/84
Sample Amount Extracted (g)			1.0618	1.0025	0
Extract Final Volume (ml)			1.0	1.0	1.0
Extract Dilution			1:1	1:1	1:1
ESC Extract or Sample Number			PCB451	PCB452	PCB455
Date of CGC/MS Analysis			6/19,6/20	6/19,6/20	6/19,620
MS FRN			19413,19422	19414,19423	19415,19424

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.
N - 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) NQ - Not Quantitateable. The congener concentration is below the LOQ value.

Table stored in file: 840718:MH:18

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

Analyst Approval: B. Mason Hughes

MONS 220773

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

ESC Standard Extraction Method (SEM) TITLE: PCBs in matrices containing acidic groups

ESC Standard Extraction Method No: PCEX07

MATRI(X).(CES):	TYPICAL SAMPLE SIZE (g)	TYPICAL EXTRACT VOLUME (ml)
carboxylic acids, chlorophenols, and any alkyl or aromatic compound that is acidic in nature	0.5 - 5g	1 - 10

TYPICAL ANALYTES: A1242,A1248,A1254,A1260,and PCB isomers mono- through deca-chloro-biphenyl.

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 characteristic mass responses as PCB isomers for MSAN03.

TYPICAL SURROGATES	TYPICAL RECOVERIES (%)
pentachlorobenzene	50 - 120
2,4,6-trichloro-biphenyl	50 - 120
3,3',4,4'-tetrachloro-biphenyl-d6	50 - 120

APPARATUS AND MATERIALS:
Burdick and Jackson hexane for sample extraction.
Potassium hydroxide solution (2 M) to ionize acidic functional groups.
Distilled deionized water for dilution of the potassium hydroxide.
Potassium hydroxide pellets.
Silica gel columns impregnated with potassium permanganate, sulfuric acid, and potassium hydroxide.
Disposable glassware.

LIMITATIONS: Method applies only to matrices which are hydrolizable using a 2M potassium hydroxide solution. EC SAMs are valid for CL3-BP through CL10-BP. MS SAMs are valid for all PCBs from CL1- through CL10-BP.

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

DATES OF METHOD CREATION AND UPDATES: 5/14/84, 6/20/84

MONS 220775

FLOW SHEET PCFS07

FOR ESC EXTRACTION METHOD PCEX07

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

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

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

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

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

---------- [ ] RINSE COLUMN WITH 2 X 20 mL HEXANE

ADD 15 mL 2 M KOH SOLUTION TO VIAL [ ]

SHAKE UNTIL SOLID IS INTO SOLUTION [ ]

EXTRACT 3 X 5 mL HEXANE [ ] [ ] [ ]

REDUCE SAMPLE VOLUME TO 1-2 mL WITH NITROGEN AND APPLY TO COLUMN QUANTITATIVLY. [ ]

ELUTE WITH 30 mL HEXANE [ ]

NITROGEN BLOW DOWN TO 1 mL [ ]

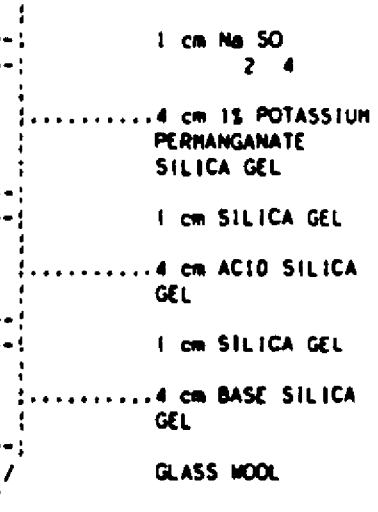
EXTRACT NO: ----------

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

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

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

CLEAN-UP COLUMN DESCRIPTION
25 mL DISPO PIPET



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ESC Standard Analysis Method (SAM) — ESC Standard Analysis Method No: MSAM03

TITLE: Organic Compounds in Solvents

ANALYTICAL INSTRUMENT AND MODE OF OPERATION: HP-5985B Capillary GC/MS-Selected Ion Monitoring with Revision-E Multi-drive software.

Typical Run Time:	3 - 40 min.
Typical Multiplier Voltage:	1800 - 2800 eV
Typical Dwell Times:	200 - 500 msec/mass
Maximum # of Masses:	20
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. Since the above referenced analytical instrument can monitor no more than 20 masses in a single analysis, incidental PCB analyses require two injections of each sample in order to analyze from CL-biphenyl through CL10-biphenyl isomers, anthracene-d10 and the surrogate spiking compound. The following summarizes the masses and approximate retention time regions monitored in these two capillary GC/MS-SIM analyses.

ANALYSIS #1

Analyte	Masses	Retention Times (minutes)
CL-BP isomers, anthracene-d10	188,190	11 - 21
CL2-BP isomers	222,224	11 - 21
3,4,3',4'-CL4-BP surrogate	296,298	21 - 28
CL5-BP isomers	323.9,325.9	21 - 28
CL7-BP isomers	391.8,393.8	28 - 39
CL9-BP isomers	461.6,463.6	28 - 39

ANALYSIS #2

anthracene-d10	186,188	14 - 23
CL3-BP isomers	255.9,257.9	14 - 23
CL4-BP isomers	289.8,291.8	23 - 29
CL6-BP isomers	357.8,359.8	23 - 29
CL8-BP isomers	427.7,429.7	29 - 39
CL10-BP isomers	497.6,499.6	29 - 39

CALCULATIONS: Analyte concentration = (Analyte area)/(Analyte RRF)(area of IS)

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)/(conc. of analyte)(area of IS)

PCB concentrations are calculated in one of two ways:

1) If an Aroclor formulation can be identified from the patterns of PCB isomers, seleted 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 in the above RRF equation. The RRFs for the corresponding PCB isomer classes are used to calculate total PCB isomer concentrations in unknown samples.

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

DATES OF METHOD CREATION AND METHOD UPDATES: 12/9/83

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

MRC ENVIRONMENTAL SCIENCES CENTER

ANALYSIS REQUEST

DATE: FEBRUARY 9,1984 LOG NO: 1-84-02-08-02

REQUESTER: PROJECT NO:
PYSZ/IVORY 484.40715, 484.40718

REPORT RESULTS TO: FILES/MEES.IVORY,BROOKS

ANALYSIS REQUESTS SENT TO: FILES,MILEMAN,IVORY,BROOKS

SAMPLE PICKUP BY: MILEMAN

SAMPLE LOCATION:LAB 28 BUILDING 2

SAMPLE DESCRIPTION FOR 1 SAMPLE

SAMPLE IDENTIFICATION	NUMBER OF BOTTLES	ESC NUMBER(S)
TETRATHAL R TCPA 831.04 (TETRACHLORO PHTHALIC ANHYDRIDE)	1	PCB-451,PCB-452-DUP PCB-453-LS,PCB-454-HS
METHOD BLANK		PCB-455

RECORDED BY: P. MUPP

REQUIRED ANALYSES: PCB,CHLORINATED BENZODIOXINS

ANALYTICAL TECHNIQUES:

	DATE COMPLETED
GC/MS (18)	6/20/84

QUALITATIVE: YES SEMIQUANTITATIVE: QUANTITATIVE: YES

REQUIRED QA/QC: SAMPLE DONE IN DUPLICATE AND A LOW AND HIGH NATIVE SPIKE

COMPLETION DATE REQUESTED: 6/22/84

COMMENTS:

SAMPLE DISPOSITION: X HOLD FOR 30 DAYS

SAFETY PRECAUTIONS: POSSIBLE PCB AND DIOXIN

ANALYSIS REQUEST FILE NAME: AA4070:L1

MONS 220780

The following is a detailed discussion of the Incidental PCB Regulation.

MONS 220781

Analysis of Incidental PCBs in Monsanto Products, Waste Streams, Emissions and Effluents of Closed and Controlled Waste Manufacturing Processes

B. Mason Hughes
Environmental Sciences Center
Monsanto Company/Dayton Laboratory
1515 Nicholas Road
Dayton,Ohio 45407

The October 21, 1982 Federal Register (Vol. 47, No. 204) contains a very extensive definition of PCB-containing products, waste streams, emissions and effluents from manufacturing processes and general descriptions of methods which should be used for these analyses. The purpose of this present report is to outline the approach taken by Monsanto's Environmental Sciences Center in supplying analytical data which can be used for certification of Monsanto products, waste streams, emissions and effluents.

In order for the material to be certified as not containing PCBs, the EPA set various Levels of Quantitation (LOQ), below which a product, waste stream, emission or effluent could be certified to contain no PCBs. The LOQ is defined on the basis of the concentration per resolvable chromatographic peak. Quoting from page 46986 of the Federal Register, Vol. 47, No. 204, "This means that for a process to be eligible for exclusion under the closed and controlled waste process exclusion, no single peak on a gas chromatogram registers PCBs in excess of: ten micrograms per cubic meter in air emissions, 100 micrograms per liter in water effluents, and two micrograms per gram in products and uncontrolled waste streams." Therefore there are very specific definitions which Monsanto can apply to its products, waste streams, emissions and effluents which determine whether these materials may be eligible for exclusion. It is the goal of the Environmental Sciences Center to supply Monsanto plants with the proper data and documentation for this exclusion.

Capillary gas chromatography/electron impact mass spectometry (CGC/MS) is the instrumental technique which the Federal Register suggests should be used in the analytical method for PCB congener analysis. However for most Monsanto products, waste streams, air emissions and water effluents, this instrumental method must be used in conjunction with an extraction method in order to determine what levels of PCB congeners, if any, are present in these various materials. The remainder of this report will therefore deal with how ESC will implement this instrumental method for the analysis of PCBs in various types of samples.

In order to analyze a sample for PCBs, using CGC/MS techniques, a representative sample of interest, or a representative extract of a sample of interest must be injected into the capillary chromatographic system. The presence and quantitites of PCB congeners present are determined by comparing the PCB congener responses in the sample of interest with the

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responses in an analytical standard containing at least one PCB congener for each of the ten chlorine classes (i. e. CL1-biphenyl through CL10-biphenyl). The analysis of Monsanto products and waste streams can be devided into two types of CGC/MS analyses. The first is for products and waste streams which can be chromatographically resolved from CL1-biphenyl through CL10-biphenyl congeners, when the product or waste stream is present at ten million times the levels of the PCB congeners. This first type of analysis only requires the sample to be injected into the CGC/MS instrument and PCB congener areas compared to standard PCB congener areas.

The second type of analysis applies to Monsanto products and waste streams which cannot be chromatographically resolved from PCB congeners and for air emission and water effluent samples. This second type of analysis must first isolate into a solvent all PCB congeners which are present in a representative sample of the product, waste stream, air or water sample. This extracting solvent can then be analyzed for PCB congeners as described above in the first type of analysis, since the extracting solvent is chosen to be chromatographically resolved from the PCB congeners of interest. Therefore an integral part of the PCB congener analysis revolves around the validation of the extraction method used to isolate the PCB congeners and validation of the CGCMS method used to analyze extracts. In order for Monsanto plants to understand the data that is generated for incidental PCB certification, the following sections outline how data will be obtained and validated for the presence or absence of PCB congeners in various Monsanto materials.

Extraction of products, waste streams, air emissions and water effluents:

If samples of interest cannot be directly analyzed for PCBs using CGC/MS techniques, they must first be extracted with an appropriate solvent which can be analyzed for PCBs. This not only applies to the products or waste streams, but also to air samples or water samples which may contain large amounts of products and waste stream components. Two major properties differences of PCBs and major compounds in samples of interest can be used to isolate PCB congeners into an appropriate extraction solvent. These are: 1) reactivity; and 2) water solubility. Low levels of quantitation for PCB congeners in samples which contain major components in the PCB congener elution region cannot easily be obtained unless these major components can be removed by their reactivity or water solubility. The inherent stability of PCB congeners and their high affinity for organic solvents and low water solubility are chemical and physical properties which can be exploited for this separation. However it is important to demonstrate that, during this isolation phase, PCB congeners have not been removed during the process. This is done in two ways. The first way involves the use of a surrogate compound which acts exactly like PCB congeners, yet is mass spectrometrically different. This is normally accomplished by using either deuterated PCB congeners or congeners which contain carbon-13 rather than carbon-12 in the biphenyl structure. These surrogate spiking compounds are added to each sample for which PCB congener extraction is required, and their recovery is reported along with any PCB congener detected. However this approach is valid only if one has isotopically labelled PCB congeners for each congener class. Since at this time there are no surrogate compounds for all classes of PCB congeners (i. e. CL1-biphenyl through CL10-biphenyl), a second type of extraction validation is normally used. This validation step involves adding at least one native PCB congener for CL1-biphenyl through CL10-biphenyl congeners and measuring the recoveries of each of these native congeners when the product, waste stream, air emission or water effluent is extracted. These native spiking studies should be performed on representative types of matrices to demonstrate the validity of the

results. If no previous data is available for recovery or all PCB congener types from a specific matrix, this native spike should be performed in order to validate the data being reported.

Since it is not anticipated that incidental PCB generation will be detected for Monsanto processes, it is imperative that the above quality control steps be conducted on each sample or for each sample matrix type in order to validate the fact that if PCB congeners had been present in the Monsanto samples, they would have been detected at the levels required by this regulation.

CGC/MS analysis of extracts, products and waste streams:

As mentioned above, sample extracts, products and waste streams can be injected directly into the CGC/MS analytical system if the major components do not elute in the retention time regions of the CL1-biphenyl through CL10-biphenyl congeners. Data quality of this analysis step is also demonstrated by similar approaches outlined above for sample extraction. In order to verify that the instrument is functioning properly for each sample injected, an internal standard is added to each extract, product or waste stream before it is injected into the CGC/MS system. Anthracene-d10 is usually used for this purpose. The absolute areas of the internal standard in the extract, product or waste stream analysis must be within 30% of the area of the internal standard which is added to the PCB congener analytical standard.

This analytical standard, containing CL1-biphenyl through CL10-biphenyl congeners, is analyzed under the same conditions as the extract, product or waste stream samples and from the instrument responses for the ten PCB congener classes, levels of detection and quantitation are determined and the amounts of each congener class (if greater than the LOQ) is reported. Ideally, each sample should also be analyzed after spiking with at least one native PCB congener in each congener class at the level of quantitation (LOQ) in order to verify that the LOQ concentration could be detected and quantified in the presence of sample interferrences. This is done in order to show that the CGC/MS instrumental analysis is valid for the sample matrix of interest. However some products and waste stream samples are not miscible with solvents in which PCB congener classes have been prepared and therefore it is not always possible to analyze a native spike of all products and waste stream samples. This is not a problem with sample extracts, since the extracting solvent has been chosen to be compatible with surrogate and native spiking studies which occur in the sample extraction step, described above.

Quantitation and Identification of PCB Congeners:

Tables 1 and 2 show how the 209 PCB congeners are distributed among the CL1-biphenyl through CL10-biphenyl classes. In addition these tables show the characteristic masses and theoretical relative abundances for each of the ten congener classes. In order to routinely obtain analytical data with levels of detection on the order of 0.1 ug/ml per congener, the mass spectrometer detector is operated in the Selected Ion Monitoring mode (SIM). This mode is a screening mode and monitors at least two molecular ion characteristic masses over the elution time region of the corresponding PCB congener class for all ten congener classes.

PCB congeners are tentatively identified from the ratio of the peak areas of the two molecular ion chromatograms. If the ratio agrees within

30% of the experimental ratio obtained from the PCB congener standard analysis, and the two peaks maximize within two mass spectrometer scans, then the sample is reanalyzed while monitoring all masses of interest for positive identification of the PCB congener. If the peak area ratio does not agree within 30% of the experimental ratio for a particular PCB congener, then this response is not due to a PCB congener.

Summary:

The above approach allows for rapid, routine analyses of extracts and samples of interest. Since few positives are expected, adequate quality control involving the use of internal standards, native spikes and surrogate spikes will be used to validate that the data can be used for the certification of the absence of incidental PCBs in Monsanto products, waste streams, air emissions and water effluents of closed and controlled waste manufacturing processes.

Text File: INPC01:MH:SP
Table Files: INTB01:MH, INTB02:MH

Table 1. Characteristic masses and isotope patterns of the characteristic masses for chlorobiphenyl through pentachlorobiphenyl congeners.

Characteristic Masses	Number of Chlorines	PCB Congener Class (Number of Congeners) CL1-BP (3)	CL2-BP (12)	CL3-BP (24)	CL4-BP (42)	CL5-BP (46)
152	0	x(-)	x(-)			
153	0	x(-)				
186	1	-		x(100)		
187	1		x(100)			
188	1	x(100)		x(32.4)		
189	1		x(32.4)			
190	1	x(32.4)		-		
220	2		-		x(100)	
222	2		x(100)		x(64.8)	
224	2		x(64.8)		x(10.5)	
226	2		x(10.5)		-	
253.9	3			-		x(100)
255.9	3			x(100)		x(97.2)
257.9	3			x(97.2)		x(31.5)
259.9	3			x(31.5)		-
287.8	4				-	
289.8	4				x(77.2)	
291.8	4				x(100)	
293.8	4				x(48.6)	
295.8	4				x(10.5)	
321.8	5					-
323.8	5					x(61.7)
325.8	5					x(100)
327.8	5					x(64.8)
329.8	5					x(21)

Table 2. Characteristic masses and isotope patterns of the characteristic masses for hexachlorobiphenyl through decechlorobiphenyl congeners.

		PCB Congener Class (Number of Congeners)				
Characteristic Masses	Number of Chlorines	CL6-BP (42)	CL7-BP (24)	CL8-BP (12)	CL9-BP (3)	CL10-BP (1)
287.8	4	x(77.2)				
289.8	4	x(100)				
291.8	4	x(48.6)				
293.8	4	x(10.5)				
321.8	5		x(61.7)			
323.8	5		x(100)			
325.8	5		x(64.8)			
327.8	5		x(21)			
329.8	5		-			
355.8	6	-		x(51.4)		
357.8	6	x(51.4)		x(100)		
359.8	6	x(100)		x(81)		
361.8	6	x(81)		x(35)		
363.8	6	x(35)		-		
389.7	7		-		x(44.1)	
391.7	7		x(44.1)		x(100)	
393.7	7		x(100)		x(97.2)	
395.7	7		x(97.2)		(17)	
397.7	7		x(17)		-	
423.7	8			-		x(34)
425.7	8			x(34)		x(88.2)
427.7	8			x(88.2)		x(100)
429.7	8			x(100)		x(64.8)
431.7	8			x(64.8)		x(26.2)
433.7	8			x(26.2)		-
459.6	9				x(26.5)	
461.6	9				x(77.2)	
463.6	9				x(100)	
465.6	9				x(75.6)	
467.6	9				x(36.7)	
493.6	10					x(21.2)
495.6	10					x(68.6)
497.6	10					x(100)
499.6	10					x(86.4)
501.6	10					x(19)

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

Copy Number: _____

GOOD LABORATORY PRACTICES MANUAL

A Guide to Quality Control/Quality Assurance

Ultratrace Analysis Group

March 1984

Joseph J. Brooks
Group Leader, Ultratrace Analysis

H. A. Wolternann
Manager, Environmental Sciences Center

Issued to: _____

Date: _____

Environmental Sciences Center
Dayton Laboratory
Dayton, Ohio 45407

JBJ/JOB A

MONS 220789

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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 (LAMs). SPMs and LAMs 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 LAM. 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 (LAMs). 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 of use, customer needs and

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 seperately.

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

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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

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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

MRC-DA
№ 156047

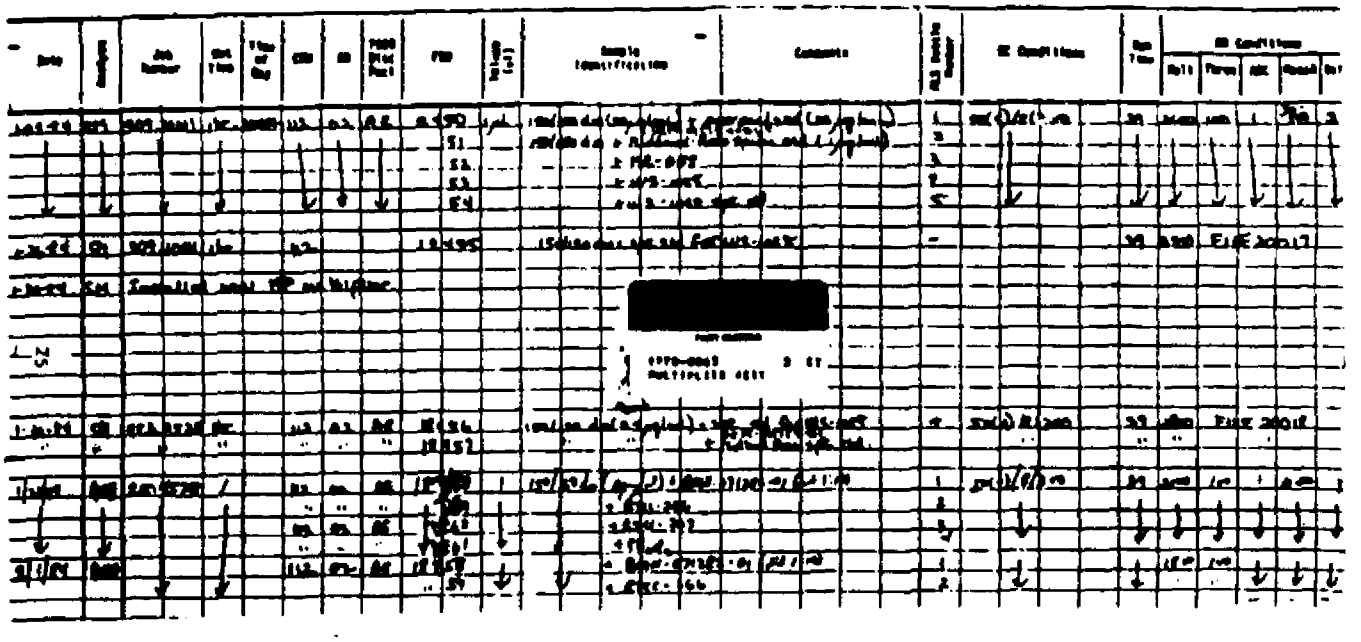

FIGURE 1. Example of GC/MS Logbook page.

HP 5880 GC/EC

MRC-DA
Nº 156363

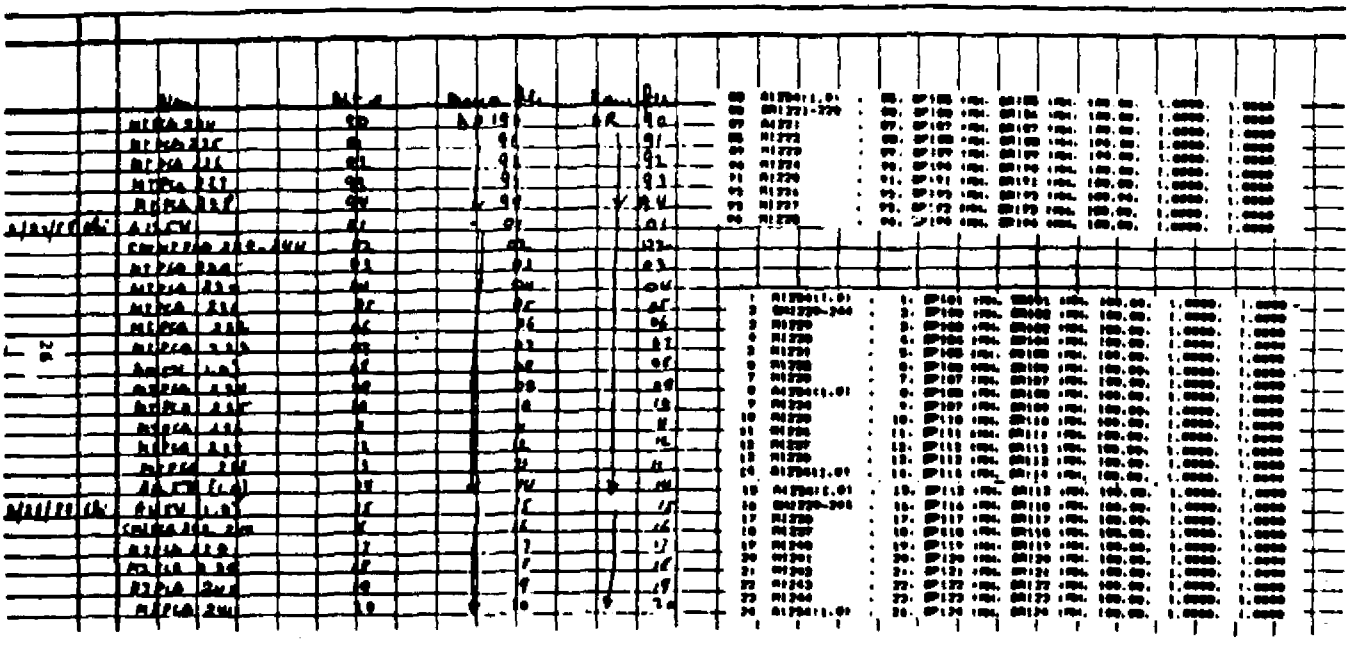

FIGURE 2. Example of GC/EC Logbook page.

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

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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 accepted value for the analyses to be considered valid. 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.

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.

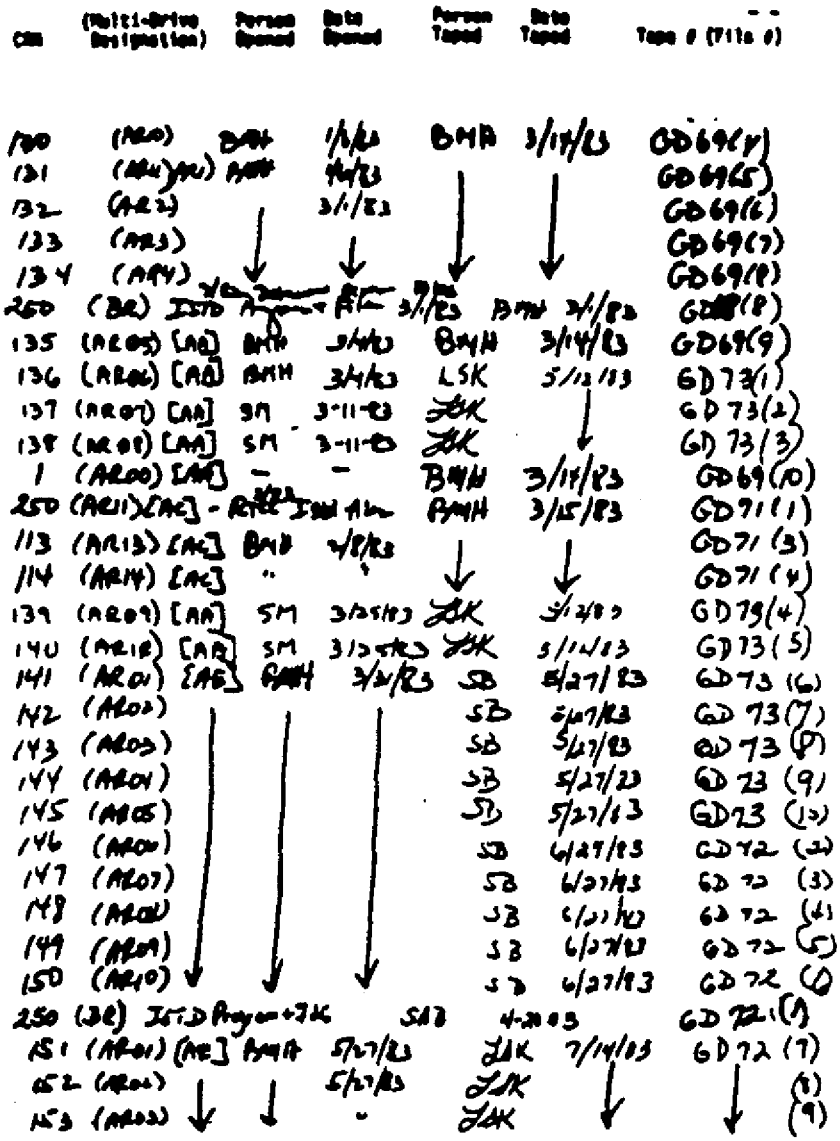

FIGURE 3. Example of DISC/Tape Logbook page.

ANALYSES FOR PCDD'S

MONS 220802

INTRODUCTION

A sample of Tetrathal was received for the analysis of polychlorinated dibenyo-p-dioxins (PCDDs). The sample was assigned log #1-84-02-08-02.

SAMPLE PREPARATION

Samples were prepared for analysis by dissolving 5 grams of the Tetrathal in 50 mL of 1 N KOH. The basic solution was extracted twice with 40 mL of hexane by shaking the mixture for 15 minutes. The combined hexane fractions were washed with 50 mL of organic free water and the water removed and the hexane dried over anhydrous sodium sulfate.

The hexane was then concentrated to 10 mL and then placed on the head of a mixed phase column consisting of (top to bottom) 2 g of silica, 4 g of silica plus 40% sulturic acid, 1 g of silica, 2 g of silica plus 36% potassium hydroxide and 1 g of silica. The column was eluted directly onto a column containing 2.5 g of Woelm basic alumina. The alumina column was first eluted with 10 mL of 2% methylene chloride/hexane (v/v) and this fraction discarded. An additional elution was made with 15 mL of a 50% methylene chloride/hexane (v/v). This second fraction was saved and concentrated to 50 µl and submitted for GC/MS analysis.

ANALYSIS

The GC/MS analyses were carried out on a Hewlett Packard 5985B. A 30 meter DB-5 fused silica capillary column was used for all gas

chromatographic separations. The mass spectrometer was operated in the selected ion monitoring mode analyzing for ion characteristic of the various PCDDs.

RESULTS

The results of the analyses are given in Table 1. Note that the results are reported as the sum of all isomers for a given degree of chlorination. No results are reported for monochlorodibenzo-p-dioxins since substantial interferences prevented the quantition of these PCDDs even at the ppm level.

TABLE 1. ANALYSIS OF TETRATHAL FOR POLYCHLORINATED DIBENZO-P-DIOXINS.

ng PCDD/gm SAMPLE (ppb)

SAMPLE	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}
Tetrathal	ND*	ND	ND	ND	2.4	33	125
Tetrathal (Rep)	ND	ND	ND	ND	2.7	37	120
Method Blank	ND	ND	ND	ND	ND	ND	ND
Method Detection Limit	1	1	1	1	1	1	1
Spike Level	2.5	2.7	2.0	2.4	2.3	2.5	2.0
Tetrathal (Spike)	1.7	2.2	1.4	2.6	4.6	42	138
Recovery %	68	82	70	108	87	-	-
Spike Level	25	27	20	24	23	25	20
Tetrathal (Spike)	7.7	17	11	16	18	51	129
Recovery %	31	63	55	67	67	64	-

*ND = none detected at the method detection limit

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