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TITLE: SUMMARY OF IMPROVEMENTS IN INCIDENTAL PCB ANALYSIS APPROACHES

AUTHORS: D. E. McKenzie, L. R. Minor and B. M. Hughes

ABSTRACT: Significant improvements were made in incidental PCB analyses using capillary GC/MS analysis methods. These improvements do not significantly lower the detection limits for these compounds, but greatly improve the documentation and efficiency of these analyses. An automated method was developed which transfers raw analyte area and characteristic/confirming ion ratio information from the HP-1000 GC/MS data system to a LOTUS 1-2-3 template file on a personal computer. This template file calculates relative response factors, surrogate recoveries, native recoveries, and produces graphs which display ion ratios. A PCB congener mixture was purchased which is routinely used to show the analysis windows for the CL1-biphenyl through CL9-biphenyl isomers. A second capillary column was evaluated for the analysis of complex PCB formulations, and several different cleanup methods were used for low-level PCB analyses.

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APPROVAL DATE: December 29, 1987

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RESEARCH REPORT

DATE: December 18, 1987

PROJECT NO: 760.24-710

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Title: Summary of Improvements in Incidental PCB Analysis Approaches.

ABSTRACT

Significant improvements were made in incidental PCB analyses using capillary GC/MS analysis methods. These improvements do not significantly lower the detection limits for these compounds, but greatly improve the documentation and efficiency of these analyses. An automated method was developed which transfers raw analyte area and characteristic/confirming ion ratio information from the HP-1000 GC/MS data system to a LOTUS 1-2-3 template file on a personal computer. This template file calculates relative response factors, surrogate recoveries, native recoveries, and produces graphs which display ion ratios. A PCB congener mixture was purchased which is routinely used to show the analysis windows for the CL1-biphenyl through CL9-biphenyl isomers. A second capillary column was evaluated for the analysis of complex PCB formulations, and several different cleanup methods were used for low-level PCB analyses.

INTRODUCTION

During 1987, significant improvements were made to ESC's Incidental PCB Analysis method. These improvements were funded through Core Research Funding of Project Number 760.24-710. The present report is a Research Report which briefly summarizes how 0.1 person-years of core funding were expended. Figure 1 summarizes the various projects which were indirectly affected by this support. Although not specificially shown, approximately 20% of this support was devoted to training of new employees who were involved in PCB analyses. It is estimated that the remaining 80% of support was devoted to research studies described in the following sections of this report.

(continued)

Appendix A summarizes the mass spectrometric instrumental analysis method which has evolved over several years of incidental PCB analysis research. In addition, this appendix describes three specialized extraction methods which were developed this year. Appendix B gives a brief description of the Incidental PCB regulation, from the perspective of the analyst who must conduct these studies. The following paragraphs discuss the contents of the remaining appendices in this research report.

MASS SPECTROMETER TUNING AND CHROMATOGRAPHIC DOCUMENTATION

An overall approach was developed to routinely evaluate how the mass spectrometer was electronically tuned, and the chemical condition of the capillary column used to separate the various PCB congeners. A system performance standard is routinely analyzed and a procedure file named SYSPRF is used to automatically evaluate data from analysis of this standard solution. Appendix C gives a listing of this procedure file and an example of output generated from its use. This standard contains 2,6-dimethylphenol, 2,6-dimethylaniline, decanol, pentachlorophenol, anthracene-d10, 1-octadecene, n-octadecane, decafluorotriphenylphosphine (DFTPP), eicosane, heneicosane, pyrene, methyl stearate, and chrysene. These components have widely varying basicities and acidities and DFTPP and pentachlorophenol have mass spectral and chromatographic properties which EPA has defined in detail in their 625 and 1625 priority pollutant methods.

The mass spectrometer tuning is evaluated by comparing the obtained spectrum for DFTPP with EPA's definition of what criteria are acceptable for this compound. The first output shown in Appendix C shows how ESC's DFTPP spectrum compares with EPA's Criterion for this compound.

Chromatographic performance is evaluated by observing the relative heights of the first two components which are 2,6-dimethylphenol and 2,6-dimethylaniline. Significant differences in the heights of these two peaks indicates that there is significant tailing for either or both of these compounds and that corrective measures should be taken. Tailing of decanol, pentachlorophenol, or chrysene are also indications that column activity is high and should be corrected. Finally, the resolution between anthracene-d10, 1-octadecene and n-ocadecane, and between pyrene, heneicosane, and methyl stearate demonstrate the reactivity of the column. Normally, these two triplets should be baseline resolved or corrective action should be taken.

(continued)

MASS SPECTROMETER CALIBRATION AND DATA ANALYSIS

Once the mass spectrometer and capillary column have been shown to be functioning properly, a standard containing PCB congeners from CL1-biphenyl through CL10-biphenyl are injected while scanning the mass spectrometer using the selected ion monitoring mode of scanning. The instrumental analysis method MSAN25, which is summarized in Appendix A, describes the masses and approximate mass windows which are monitored for Incidental PCB analysis. The instrumental scanning method, PCSC25, is also shown in this appendix. One important advancement in the analysis of PCB congeners is shown in Appendix D. Table D-1 shows Internal Standard, and Surrogate and Native Spiking Compounds which are used in the analysis of incidental PCBs. In addition, Appendix D shows a listing of the procedure file named PCCALC which is used to automatically produce high quality graphic outputs which can be used to easily evaluate whether various responses are likely due to PCBs. This output is shown following the listing and a typical ASCII file is also shown which can be transferred to a personal computer LOTUS template file. This LOTUS file was designed to calculate relative response factors, and other important quantitative formation relating to data analysis. Tables 1, 1a, 1b, and 2 are examples of tables which are automatically generated from this LOTUS template file.

Appendix E shows another type of procedure file which is used to analyze for all PCB congeners with a certain number of chlorine atoms. This proceedure file output reports total PCB isomers within a certain window. In order for responses to be summed in this total, retention times of the characteristic and confirming mass chromatographic peaks must be within 10 seconds of one another.

PCB WINDOW STANDARD

The final instrumental improvement in ESC's Incidental PCB Analysis Protocol includes the use of a PCB Window Standard from Wellington Laboratories. Table F-1 in Appendix F shows specific isomers which are present in this standard and Figures F-1a and F-1b show ESC's chromatogram obtained from the analysis of this standard. This appendix also shows the output generated from the proceedure file named PCWNDW. Following this output are documentation from Wellington Laboratories and Figure F-2 which shows the chromatogram obtained by Wellington Laboratories from GC/MS analysis of this PCB Window Standard. The analysis of this standard gives good documentation that the proper retention time windows were scanned so that if any of the 209 PCB congeners had been present in a sample extract above the level of detection, it would have been identified.

(continued)

EVALUATION OF BIPHENYL CAPILLARY COLUMN

Recently capillary columns containing a polysiloxane/biphenyl stationary phase have become available commercially from Lee Scientific (Salt Lake City, UT). ESC has traditionally used J&W (Folsom, CA) DB-5 polysiloxane/phenyl capillary columns for PCB analysis. The use of a biphenyl SB-30 column for PCB analysis was investigated because the stationary phase (biphenyl) and PCBs (polychlorinated biphenyls) have similar polarities, which could possibly impart greater chromatographic selectivity in analyses. This hypothesis was tested by installing a biphenyl capillary column (25 m, SB-30, 0.32 mm diameter, 0.25 um film thickness) into the same Hewlett-Packard 5880 gas chromatograph that is used for PCB analysis equipped with a J&W (30 m, DB-5, 0.32 mm diameter, 0.25 um film thickness) capillary column.

The normal operating conditions for DB-5 column PCB analysis use a 5 psi head pressure, an oven temperature profile of 130(1)/4/300, and splitless injection. The oven temperature profile was changed to 130(1)/5/300 for the SB-30 column PCB analysis because of the longer retention times observed using this column.

Appendix G contains Figures G-1 through G-3 which show chromatograms obtained on the DB-5 and the SB-30 column. Figure G-1 shows four Aroclor formulation chromatograms obtained on a DB-5 capillary column using an electron capture detector (ECD). Figure G-2 shows five Aroclor formulation chromatograms obtained on an SB-30 capillary column. Figure G-3 shows (from bottom to top) Aroclor 1248, a sample which was known to contain chromatographic interferents, Aroclor 1248, and the same sample known to contain interferents. The bottom two chromatograms were obtained on the SB-30 column, and the top two chromatograms were obtained on the DB-5 column. Both columns obviously show that the sample contains Aroclor 1248. However the beginning of the Aroclor formulation is more discernable on the SB-30 column.

Adequate resolution was obtained on both columns, although a comparison of Figures G-1 and G-2 show the formulation patterns are different. These two figures also show that the PCBs have longer retention times on the SB-30 column even though we are using a faster temperature ramp than is normally used in the DB-5 column PCB analysis.

We can conclude that the SB-30 capillary column is usable and in some cases perhaps desirable for PCB analysis. However, no better separation of PCB congeners was obtained on the SB-30 column. Since the majority of PCB analyses performed by the Environmental Sciences Center is done using pattern comparison approaches (identifying the Aroclor which is present and calculating concentrations from that Aroclor formulation), the day to day use of an SB-30 column would be required for adequate comparison of the two columns. At present there is no distinct evidence that the use of one column would offer an advantage over the other column. Analysts have experience with patterns on the DB-5 column and there are no present plans to change columns at this time.

(continued)

SUMMARY OF EXTRACTION METHODS USED

Several projects over the past year required the use of modified extraction and particularly cleanup methods for PCB analysis. ESC has been using a mixed bed impregnated silica gel column over the past several years for the removal of interferents from sample matrices. The column consists of permanganate, base, and acid impregnated silica gels through which the extract is passed. This approach has been used in conjunction with many of the instrumental improvements described earlier in this report. A brief description of this cleanup approach can be seen in Standard Extraction Method PCEX30 and flow sheet PCFS30 which are shown in Appendix A.

One set of chloronitrobenzene samples was analyzed by reduction of the nitro-group to an NH2- group by the direct addition of HCL and mossy tin to the sample matrix prior to the use of our standard silica gel mixed bed cleanup column. This approach was completely succesful and resulted in an accurate analysis with a lower limit of detection than would have been possible without this reduction step. Sample size was approximately 1 g and final extract volume was 1 mL. A brief description of Standard Extraction Method PCEX06 and flow sheet PCFS06 are shown in Appendix A.

An even more useful technique was developed for sample cleanup as a part of Monsanto's Fermentia due diligence effort. Two compounds were analyzed which were very stable and could not be hydrolized except under very harsh conditions such as concentrated sulfuric acid. The tin/HCL approach was attempted but without success. A method was finally developed which involved: 1) the use of dimethyl formamide (DMF) to dissolve the samples; 2) addition of water to the solution; and 3) extraction of the resulting DMF/water solution with hexane. Two percent water was added to decrease the PCB solubility in the DMF/water phase. It was found that without the addition of water to DMF, the distribution coefficient of the lower chlorine class PCBs (monchloro- through tetrachloro-biphenyls) was less than 0.3. Decachorobiphenyl had a distribution coefficient close to 10. (Note: The distribution coefficient is defined as {concentration of analyte in extract}/{concentration of analyte in sample/water/DMF}.) Normally, for efficient extractions, distribution coefficients are on the order of 10,000. These low distribution coefficients were unsatisfactory for efficient extractions. When water was added to the sample/DMF solution, the distribution coefficient was raised to a point where extraction efficiencies were measured between 50 and 80% for all PCB congeners. A brief description of this cleanup approach can be seen in Standard Extraction Method PCEX04 and flow sheet PCFS04 which are shown in Appendix A.

This methodology was unique since no harsh conditions were used to hydrolize the matrix, and the amount of selectivity gained was high enough to allow a 1 g sample to be placed in 1 mL of solvent. Further work should be done in the area of terniary solvent systems in order to exploit solubility differences as a means of isolating PCB congeners.

(continued)

DETAILS

Standard Extraction Method(s): PCEX04 {Also see PCFS04 for method flow sheet.)
PCEX06 {Also see PCFS06 for method flow sheet.}
PCEX30 {Also see PCFS30 for method flow sheet.}

Standard Analysis Method: MSAN25

Mass Spectrometer Data Acquisition Method: PCSC25

Mass Spectometric Tuning File: MT8602

Final Report File No(s): RA7710

Table File No(s): TA7710, TB7710, FA7710, FB7710, RB7710

APPENDICES

Appendix A. Summary of Extraction and Analysis Methods Developed.

Appendix B. Brief Description of Analysis Approaches Used in the Analysis of Incidental PCBs.

Appendix C. Listing of Procedure Files and Examples of Computer outputs Produced from the Analysis of the System Performance Standard. {SYSPRF Transfer File.}

Appendix D. Listing of PCB Congeners Used for Instrument Calibration and Procedure Files and Examples of Computer Outputs Produced in Incidental PCB Analyses. {PCCALC and PCOUTP Transfer Files.}

Appendix E. Listing of Procedure Files and Examples of Computer Outputs Produced in Incidental PCB Analyses. {PTCALC and PTOUTP Files.}

Appendix F. Listing of PCB Congers Present in PCB Window Standard and Procedure Files and Examples of Computer Outputs Produced in Incidental PCB Analyses. {PTWNDW and PTOUTP Transfer Files.}

Appendix G. Chromatograms Obtained from the Comparison of DB-5 and SB-30 Capillary Columns.

ANALYST(S): David E. McKenzie, LaShawn R. Minor and B. Mason Hughes

ANALYST APPROVAL: _____

Figure 1 – PCB Activities (Adjunct)

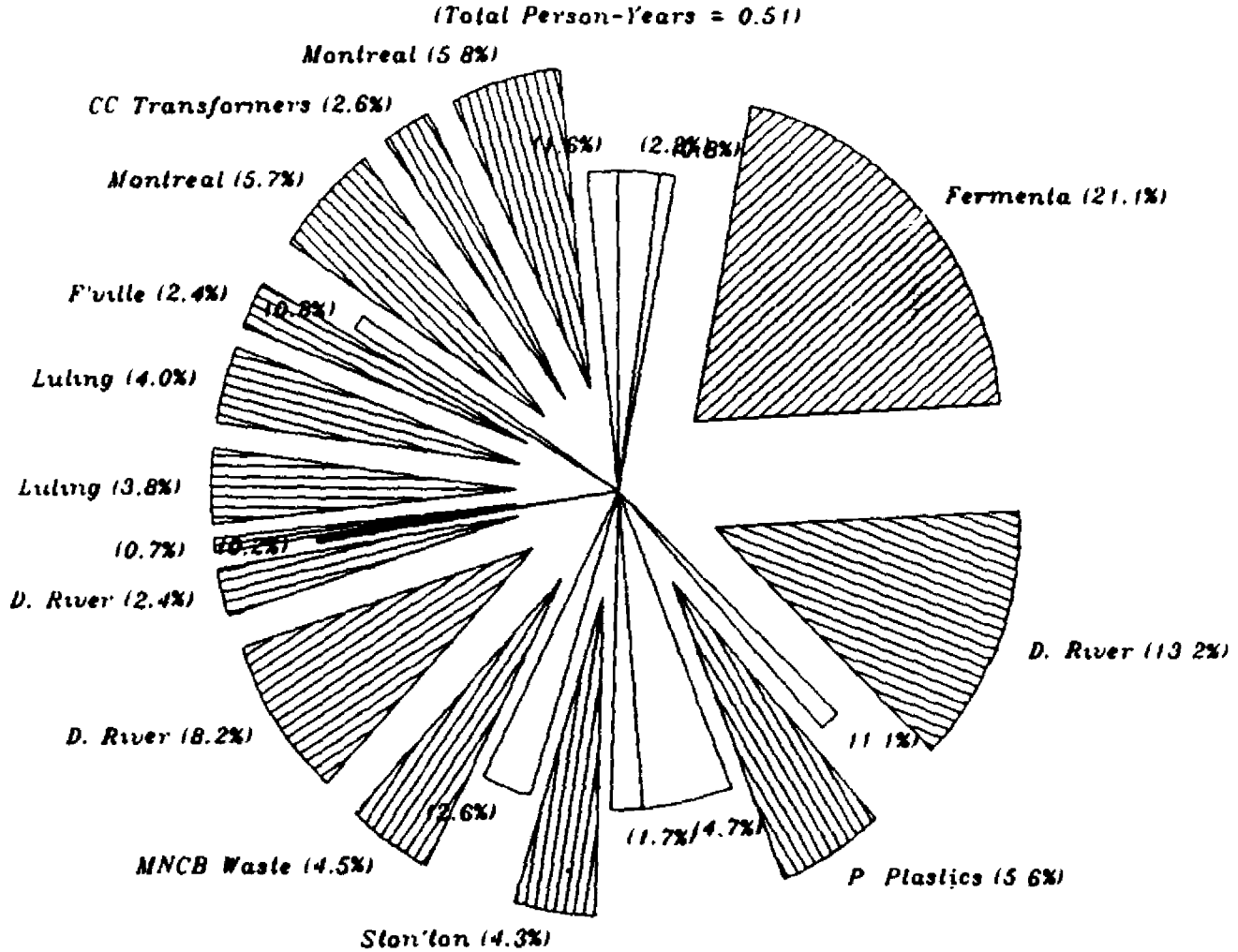

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Table 1. Example of Incidental PCB Concentration Results Automatically Generated from LOTUS 1-2-3.

Table 1 Results of Krumbrich Incidental PCB Study in Chloronitrobenzenes Using Standard Extraction and Analysis Methods PCEX06 and MSAN25 (Project: 7231)

FRMS USED FOR CALIBRATION. >L4302 >L4305 >L4309

SAMPLE ID / EXTRACT NUMBER → / CONGENER CLASS	Meta CNB PCB-2132 (ug/mL)	Meta CNB DUP PCB-2133 (ug/mL)	Crude CNB PCB-2136 (ug/mL)	Crude-CNB DUP PCB-2137 (ug/mL)	Meth Blank PCB-2140 (ug/mL)	Meta-CNB+MS PCB-2135 (ug/mL)	Crude CNB+MS PCB 2138 (ug/mL)	Meta-CNB+LS PCB-2134 (ug/mL)	Crude CNB+LS PCB-2138 (ug/mL)	MS SPK MS SP 610 (ug/mL)
Monochlorobiphenyls	0	0	0	0	0	9	7.7	2.5	2.3	0.9
Dichlorobiphenyls	0.5	0.4	1	1	0	14.5	11.2	3.2	3.7	11.2
Trichlorobiphenyls	0.1	0	0	0	0	0.1	0	2.1	2.4	0.2
Tetrachlorobiphenyls	0	0	0	0	0	7.3	7.1	1.9	2.7	7.9
Pentachlorobiphenyls	0	0	0	0	0	8.3	7.0	1.7	2.4	0.2
Hexachlorobiphenyls	0	0	0	0	0	7.0	0.7	1.9	2.0	7
Heptachlorobiphenyls	0	0	0	0	0	5.4	5.2	1.1	1.0	5.4
Octachlorobiphenyls	0	0	0	0	0	2.4	1.9	0.7	1.1	1.0
Nonachlorobiphenyls	0	0	0	0	0	2.4	2.1	0.0	1.2	1.0
Decachlorobiphenyl	0	0	0	0	0	1.5	1.1	0.9	1.5	0.0
TOTAL PCBS IN EXTRACT(ug/mL)	9.6	0.4	1	1	0	63.7	58.9	16.6	21.9	61.2
TOTAL PCBS IN SAMPLE (ug/g)	0.4	0.3	0.0	0.7	0	51.7	57.2	13.0	22.1	61.2
SUBROGATE COMPOUND	(% REC)	(% REC)	(% REC)	(% REC)	(% REC)	(% REC)	(% REC)	(% REC)	(% REC)	(% REC)
Monochlorobiphenyl-6C13	109	92	85	70	40	108	93	83	78	99
Tetrachlorobiphenyl-12C13	92	56	110	87	115	88	65	88	105	71
Octachlorobiphenyl-12C13	90	40	140	182	148	43	33	65	118	33
Decachlorobiphenyl 12C13	276	57	230	288	295	20	19	105	133	16
MS RAW FILE →	: >L4297	: >L4298	: >L4299	: >L4300	: >L4301	: >L4306	: >L4307	: >L4303	: >L4304	: >L4305
DILUTION FACTOR	0.698	0.831	0.771	0.673	1	0.012	0.973	0.832	1.01	1
SAMPLE AMOUNT (g)	1.435	1.204	1.297	1.485	1	1.232	1.028	1.202	0.99	1
EXTRACT FINAL VOLUME (mL) →	1	1	1	1	1	1	1	1	1	1
ANTHRACENE 010 (1S10) AREA →	266075	1044699	954998	1223788	1349163	941563	1142561	1207997	1209922	1234338

Note: Concentrations reported are rounded to 1 decimal place. Values of 0 should be interpreted as < 0.1 ug/g.

Table Generation Comments: ALL FILES TEST OK

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Table 1a. Example of Incidental PCB Relative Response Factor Results Automatically Generated from LOTUS 1-2-3.

Table of Average Relative Response Factors
Generated for Each Congener Class

	Characteristic Relative Response Factors			Average Response Factor	Average Congener Response
	Response from standard1	Response from standard2	Response from standard3		
Cl1 biphenyl #2	0.33	0.363333	0.42	0.371111	0.371111
Cl1 biphenyl #3	0.385	0.456666	0.51	0.463888	0.515222
Cl1 biphenyl #4	0.642	0.726666	0.823333	0.730666	
CL4biphenyl 6C13#5	0.964	1.14	1.34	1.148	1.148
CL2biphenyl #6	0.266	0.291666	0.37	0.309222	
CL2biphenyl #7	0.517	0.563333	0.696666	0.592333	0.504305
CL2biphenyl #8	0.413	0.456666	0.576666	0.475444	
CL2biphenyl #9	0.554	0.59	0.776666	0.640222	
CL3biphenyl #10	0.224	0.232	0.302666	0.252888	
CL3biphenyl #11	0.248	0.246	0.323666	0.272555	0.260111
CL3biphenyl #12	0.225	0.231	0.308666	0.254888	
CL4biphenyl #13	0.141	0.128	0.173333	0.147444	
CL4biphenyl #14	0.116	0.108666	0.148333	0.124333	0.141074
CL4biphenyl #15	0.142	0.133333	0.179	0.151444	
CL4biph 12C13#16	0.527	0.329	0.533	0.463	0.463
CL5biphenyl #17	0.0751	0.077	0.102333	0.084811	
CL5biphenyl #18	0.0616	0.069666	0.093	0.074755	0.078559
CL5biphenyl #19	0.064	0.067	0.097333	0.076111	
CL6biphenyl #20	0.0517	0.043333	0.072333	0.055788	
CL6biphenyl #21	0.0398	0.035333	0.059666	0.044933	0.0455
CL6biphenyl #22	0.0322	0.0278	0.047333	0.035777	
CL7biphenyl #23	0.0461	0.048666	0.066666	0.053811	0.054611
CL7biphenyl #24	0.0469	0.049666	0.069666	0.055411	
CL8biphenyl #25	0.0209	0.014633	0.039333	0.024955	0.024955
CL8biph 12C13#26	0.243	0.0703	0.327	0.213433	0.213433
CL9biphenyl #27	0.0232	0.016166	0.041333	0.0269	0.0269
Cl10biphenyl #28	0.0161	0.003766	0.022733	0.0142	0.0142
Cl10biph 12C13#29	0.0822	0.00936	0.0875	0.059686	0.059686

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Table 1b. Example of Incidental PCB Characteristic Ion/Confirming Ion Ratio Results Automatically Generated from LOTUS 1-2-3.

TABLE OF CHARACTERISTIC ION RESPONSES TO CONFIRMING TIMES 100 FOR SAMPLES 1-10 FOR SAMPLES IN CONCENTRATION TABLE:

Table 1 Results of Cruzmarich Incidental PCB Study in Chloronitrobenzenes Using Standard Extraction and Analysis Methods PCE806 and MSA825 (Project: 7231)

	STANDARD USED IN CALCULATIONS			FILE NAMES										MINIMUM RATIO	MAXIMUM RATIO	AVERAGE RATIO
	S1	S2	S3	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10			
COMPOUND ID	>L4302	>L4305	>L4309	>L4297	>L4298	>L4299	>L4300	>L4301	>L4306	>L4307	>L4303	>L4304	>L4305			
001 = anthracene d10	8720	8669	8520	9172	8871	8816	8744	8743	8699	8906	8852	8908	8669	8520	8720	8834
002 = CL biphenyl #1	290	294	288	323	274	230	303	160	285	295	284	284	294	288	294	291
003 = " #2	288	296	291	190	58	154	225	217	292	297	294	289	296	288	296	292
004 = " #3	292	294	285	97	241	264	261	213	288	287	292	283	294	285	294	290
005 = 4 CL biphenyl-13C12	291	298	286	300	293	301	299	297	293	299	297	299	298	291	300	298
006 = CL2 biphenyl #1	160	160	159	49	224	170	158	188	164	159	161	163	160	159	160	160
007 = " #2	159	162	157	164	164	162	165	0	160	161	162	159	162	157	162	159
008 = " #3	162	160	157	162	164	159	162	0	161	164	160	160	160	157	162	160
009 = " #4	160	162	157	152	164	156	160	0	160	161	162	161	162	157	162	160
010 = CL3-biphenyl #1	88	82	86	85	98	97	87	250	88	89	88	68	82	82	88	85
011 = " #2	91	82	85	88	78	81	107	78	82	88	87	86	82	82	91	86
012 = " #3	86	83	83	116	83	96	96	429	82	88	88	87	83	83	86	84
013 = CL4 biphenyl #1	93	94	85	220	242	763	129	126	97	96	92	88	94	85	94	91
014 = " #2	90	97	86	103	417	462	132	288	94	98	94	90	97	86	97	93
015 = " #3	90	94	86	150	121	1650	276	296	97	100	92	91	94	86	94	90
016 = CL4-BP-13C13 Surr	92	117	91	97	96	93	97	94	112	529	96	96	117	91	117	100
017 = CL5-biphenyl #1	60	59	59	126	200	575	904	229	60	60	60	58	59	59	60	59
018 = " #2	58	61	61	103	109	161	206	588	59	61	60	60	61	58	61	60
019 = " #3	60	60	62	2100	295	183	543	350	60	59	60	62	60	60	62	61
020 = CL6 biphenyl #1	57	64	58	95	147	229	447	316	65	64	57	57	64	57	64	60
021 = " #2	56	62	56	233	350	260	310	1575	63	65	58	57	62	56	62	58
022 = " #3	58	64	55	293	132	371	268	257	82	64	58	57	64	35	66	58
025 = CL7-biphenyl #1	147	150	151	200	371	73	203	95	149	153	148	149	150	147	151	149
024 = " #2	150	156	153	644	615	106	123	176	150	148	148	148	156	150	156	153
025 = CL8 biphenyl	80	71	84	205	322	208	134	140	72	78	80	85	71	71	84	78
026 = CL8 BP-13C13 Surr	81	56	83	76	77	82	80	80	65	56	75	77	56	56	85	73
027 = CL9-biphenyl	93	106	86	247	683	188	218	750	100	105	100	97	106	86	106	95
028 = CL10-biphenyl	142	215	133	231	167	109	121	140	279	206	167	146	215	135	215	177
029 = CL10-BP-13C13 Surr	163	133	152	146	157	156	155	154	137	132	173	343	153	133	163	149

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Table 2. Example of Incidental PCB Native Spiking Recovery Results Automatically Generated from LOTUS 1-2-3.

Table 2 — Native Spiking Recoveries in Krummrich Chloronitrobenzene Samples
Using Standard Extraction and Analysis Methods PCEX86 and MSAN25. (Project 7231)

MS CALIB FILE: >L4305
LS CALIB FILE: >L4302

COMPOUND ID	Matx-CMB+MS PCB-2135 (% REC)	Crude-CMB+MS PCB-2139 (% REC)	MS SPK MS SP STD (% REC)	Matx-CMB+LS PCB 2134 (% REC)	Crude-CMB+LS PCB-2138 (% REC)	LS SPK LS SP STD (% REC)
#02 = CL-biphenyl #1	105	89	100	95	89	100
#03 = " #2	102	88	100	93	87	100
#04 = " #3	100	86	100	95	88	100
#06 = CL2-biphenyl #1	104	92	100	90	95	100
#07 = " #2	98	92	100	85	89	100
#08 = " #3	107	117	100	105	149	100
#09 = " #4	103	101	100	96	99	100
#10 = CL3-biphenyl #1	96	97	100	79	89	100
#11 = " #2	102	100	100	80	85	100
#12 = " #3	99	98	100	81	95	100
#13 = CL4-biphenyl #1	95	95	100	67	95	100
#14 = " #2	88	89	100	70	95	100
#15 = " #3	94	90	100	69	95	100
#17 = CL5-biphenyl #1	105	97	100	65	90	100
#18 = " #2	100	94	100	69	96	100
#19 = " #3	102	96	100	70	90	100
#20 = CL6-biphenyl #1	105	92	100	50	93	100
#21 = " #2	111	97	100	75	107	100
#22 = " #3	121	90	100	80	112	100
#23 = CL7 biphenyl #1	100	99	100	62	106	100
#24 = " #2	101	94	100	66	110	100
#25 = CL8-biphenyl	135	110	100	65	135	100
#27 = CL9-biphenyl	135	116	100	71	134	100
#28 = CL10-biphenyl	194	142	100	75	132	100
SURROGATE COMPOUNDS						
#05 = 4-CL-biphenyl-6C13	101	94	100	99	95	100
#16 = CL4 BP-12C13 Surr	124	91	100	70	92	100
#26 = CL8 BP 12C13 Surr.	132	100	100	57	103	100
#29 = CL10 BP-12C13 Surr	120	120	100	76	97	100
MS RAW FILE =	>L4306	>L4307	>L4305	>L4303	>L4304	>L4302

LS = the addition of 0.1 ug per PCB congener.

MS = the addition of 1 ug per PCB congener.

Note - Recoveries are rounded to the nearest whole number

MONS 221122

Appendix A. Summary of Extraction and Analysis Methods Developed.

MONS 221123

ESC Standard Analysis Method (SAM) ESC Standard Analysis Method No
TITLE: Polychlorinated Compounds in Solvents MSAN25

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

Typical Run Time:	15 - 40 min.
Typical Multiplier Voltage:	1800 - 2800 eV
Typical Dwell Times:	100 - 500 msec/mass
Maximum # of Masses	20 masses x 5 ranges = 100 masses
Electron Energy:	70 eV

Mass Spectrometer Tuning File: MT8602
Mass Spectrometer Data Acquisition Method: PCSC25

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

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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

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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

(continued)

DATA ACQUISITION INFORMATION

Analyte	Masses	Retention Times (minutes)
CL-BP isomers, anthracene-d10	188,190	15 - 22
4-CL-BP-6C13 surrogate	194,196	15 - 22
CL2-BP isomers	222,224	15 - 22
CL3-BP isomers	255.9,257.9	15 - 30
CL4-BP isomers	289.8,291.8	22 - 30
3,4,3',4'-CL4-BP-12C13 surrogate	301.8,303.8	22 - 30
CL5-BP isomers	323.9,325.9	22 - 30
CL6-BP isomers	359.8,361.8	22 - 35
CL7-BP isomers	393.8,395.8	22 - 35
CL8-BP isomers	427.7,429.7	30 - 35
2,2',3,3',5,5',6,6-CL8-BP-12C13 surr.	439.7,441.7	30 - 35
CL9-BP isomers	461.6,463.6	30 - 35
CL10-BP	497.6,499.6	30 - 35
CL10-BP-12C13 surrogate	509.6,511.6	30 - 35

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 congeners 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.
(For more information regarding standards, see Supplement to MSAN25 on the following page.)

SAFETY PRECAUTIONS: See PCB handling protocols in laboratory safety manual

DATE OF METHOD CREATION: 12/9/83 Time Stamp - <871123.1532>

(continued)

Supplemental Information to Standard Analysis Method MSAN35

The following describes details of internal standards, surrogate standards, and individual PCB congeners used for instrument calibration:

Internal Standard

Anthracene-d10

Surrogate Spiking Compounds C-13 labeled

4-chlorobiphenyl 13C6
3,3',4,4'-tetrachlorobiphenyl 13C12
2,2',3,3',5,5'6,6',-octachlorobiphenyl
decachlorobiphenyl 13C12

Native Spiking Compounds (usad for native spikes and instrumental calibration)

2-monochlorobiphenyl
3-monochlorobiphenyl
4-monochlorobiphenyl
2,2'-dichlorobiphenyl
2,5-dichlorobiphenyl
2,4'-dichlorobiphenyl
4,4'-dichlorobiphenyl
2,4,6-trichlorobiphenyl
2,3,4-trichlorobiphenyl
2,4,4'-trichlorobiphenyl
2,3',4,6,-tetrachlorobiphenyl
2,3,5,6,-tetrachlorobiphenyl
2,2',4,4',-tetrachlorobiphenyl
2,2',3,4,5-pentachlorobiphenyl
2,2',3,4,5'-pentachlorobiphenyl
2,2',4,5,5'-pentachlorobiphenyl
2,2',3,3',4,4'-hexachlorobiphenyl
2,2',3,4,4',5'-hexachlorobiphenyl
2,2',3,3',6,6'-hexachlorobiphenyl
2,2'3,3',4,4',6-heptachlorobiphenyl
2,2'3,4,4',5',6-heptachlorobiphenyl
2,2',3,3',4,4',5,5'-octachlorobipyhenyl
2,2',3,3',4,5,5,',6,6'-nonachlorobiphenyl
decachlorobiphenyl

(continued)

PCB Windowing Compounds (used to document proper data acquisition windows)

3-CL1- and 4-CL1-biphenyl
2,6-CL2 and 4,4'CL2-biphenyl
2,4,6-CL3- and 3,4,4'-CL3-biphenyl
2,2',6,6'-CL4- and 3,3',4,4'-CL4-biphenyl
2,2',4,6,6'-CL5- and 3,3',4,4',5-CL5-biphenyl
2,2',4,4',6,6'-CL6- and 3,3',4,4',5,5'-CL6-biphenyl
2,2',3,4',5,6,6'-CL7- and 2,3,3',4,4',5,5'-CL7-biphenyl
2,2',3,3',5,5',6,6'-CL8- and 2,3,3',4,4',5,5',6-CL8-biphenyl
2,2',3,3',4,5,5',6,6'-CL9- and 2,2',3,3',4,4',5,5',6-CL9-biphenyl
CL10-biphenyl

Characteristic and Confirming Masses Monitored

	Characteristic (AMU)	Confirming (AMU)
anthracene-d10	188	190
4-chlorobiphenyl-6C13	194	196
3,3'4,4'-tetrachlorobiphenyl-12C13	301.8	303.8
2,2'3,3',5,5',6,6'-octachlorobiphenyl-12C13	439.7	441.7
decachlorobiphenyl-12C13	509.6	511.6
monochlorobiphenyls	188	190
dichlorobiphenyls	222	224
trichlorobiphenyls	255.9	257 9
tetrachlorobiphenyls	289.8	291.8
pentachlorobiphenyls	323.9	325.9
hexachlorobiphenyls	359.8	361.8
heptachlorobiphenyls	393.8	395.8
octachlorobiphenyls	427.7	429.7
nonachlorobiphenyls	461.6	463.6
decachlorobiphenyl	497 6	499 6

Enter the name of the method file pcsc25

M E T H O D F I L E L I S T

Method file: PCSC25 GC type. 5840 Run Type. SIM, GC, EI
Column Cap Splitless. Yes

Temperature	Source	Isothermal	Post Run Time
	200 0	N	0 0

Run time: 40.00
Scan Start time: 15.00

	ON	OFF	ON	OFF
Relay #1:	327.0	327.0	327.0	327.0
Relay #2:	327.0	327.0	327.0	327.0
Triac #0:	327.0	327 0	327 0	327.0
Triac #1	327.0	327.0	327.0	327.0

Sim Parameters: Number of groups: 3

Multiplier voltage: 2600
Emission current: 300 uA

Group 1		Group 2		Group 3		Group 4		Group 5	
Start/Stop 15.00 22.50		Start/Stop 22.50 29.50		Start/Stop 29.50 40.00		Start/Stop 0.00 0.00		Start/Stop 0.00 0.00	
M/Z	Dwell	M/Z	Dwell	M/Z	Dwell	M/Z	Dwell	M/Z	Dwell
-188.0	100	-255.9	100	-359.8	100	0.0	0	0.0	0
-190.0	100	-257.9	100	-361.8	100	0.0	0	0.0	0
-194.0	100	-289.8	100	-393.8	100	0.0	0	0 0	0
-196.0	100	-291.8	100	-395.8	100	0.0	0	0.0	0
-222.0	100	-301.8	100	-427.7	100	0.0	0	0.0	0
-224 0	100	-303.8	100	-429.7	100	0.0	0	0.0	0
-255.9	100	-323 9	100	-439.7	100	0.0	0	0.0	0
-257 9	100	-325.9	100	-441.7	100	0.0	0	0.0	0
0.0	0	-359.8	100	-461.6	100	0.0	0	0.0	0
0.0	0	-361.8	100	-463.6	100	0.0	0	0.0	0
0 0	0	-393.8	100	-497.6	100	0.0	0	0.0	0
0.0	0	-395.8	100	-499.6	100	0.0	0	0.0	0
0.0	0	0.0	0	-509.6	100	0.0	0	0.0	0
0 0	0	0.0	0	-511.6	100	0.0	0	0.0	0
0 0	0	0.0	0	0.0	0	0.0	0	0.0	0
0.0	0	0.0	0	0.0	0	0.0	0	0.0	0
0.0	0	0.0	0	0.0	0	0.0	0	0.0	0
0.0	0	0.0	0	0.0	0	0.0	0	0.0	0
0.0	0	0.0	0	0.0	0	0.0	0	0.0	0
0.0	0	0.0	0	0.0	0	0.0	0	0.0	0

MONS 221128

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

ESC Standard Extraction Method No.
PCEX04

MATRI(X).(CES)	TYPICAL SAMPLE SIZE (g)	TYPICAL EXTRACT VOLUME (ml)
Nylon, SEF fibers, water soluble matricea etc.	0.5 - 5 0	1 - 10

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 characteriatic mass responaes as PCB isomers for MSAN03.

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

APPARATUS AND MATERIALS:
Burdick end Jackson hexane for sample extraction.
Water soluble solventa auch aa dimethyl formamide, water, basic water, methanol, ethanol, acetic acid or others.
Sodium sulfate to dry the sampla matrix.
Silica gel columns impregnated with potassium permenganate, sulfuric acid, and potaasium hydroxide.
Disposeble glasaware.
Nitrogen for extract volume reduction.
(See flow sheet for this extraction method in PCFS04.)

LIMITATIONS: Method applies only to matrices which contain hydrolizable electron capturing species in the trichlorobiphenyl through octachlorobiphenyl iaomer retention time region for EC detection methods.

SAFETY PRECAUTIONS: See PCB handling protocols in leboratory safety manual

DATES OF METHOD CREATION AND UPDATES: 10/25/83, 9/25/84

MONS 221129

FLOW SHEET PCFS04

FOR ESC EXTRACTION METHOD PCEX04

SAMPLE ID: ..... MRC EXTRACT # .....

..... LOG NO: .....

EXTRACTION DATE and TIME: .....

WEIGH OUT SAMPLE INTO A 40 mL VIAL [ ]

FINAL WEIGHT .....

INITIAL WEIGHT .....

SAMPLE WEIGHT .....

SPIKE 100 uL [ ]

ADD 15 mL WATER SOLUBLE SOLVENT (FORMIC ACID FOR NYLON, VYDYNE ECT, DIMETHYL FORMAMIDE FOR SEF FIBERS) [ ]

EXTRACT 3 X 3 mL WITH HEXANE [ ] [ ] [ ]

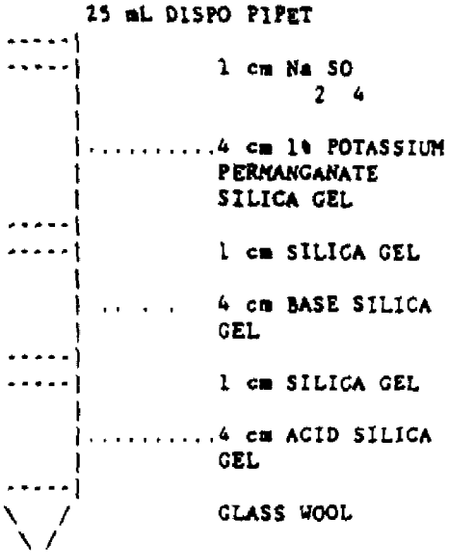
APPLY EXTRACT TO COLUMN QUANTITATIVELY [ ]

ELUTE SAMPLE INTO 50 mL CENTRIFUGE TUBE WITH 40 mL HEXANE. [ ]

NITROGEN BLOW DOWN TO 1 mL [ ]

[ ] RINSE COLUMN WITH 2 X 20 mL HEXANE

CLEAN-UP COLUMN DESCRIPTION
25 mL DISPO PIPET



EXTRACT NO: .....

DATE/TIME COMPLETED .....

ANALYST: .....

ESC JOB NO: .....

MONS 221130

ESC Standard Extraction Method (SEM) TITLE PCBs in nitro group containing matrices

ESC Standard Extraction Method No PCEX06

MATRI(X),(CES)

p-nitrophenetol, aromatic/ alkyl nitro containing compounds.

TYPICAL SAMPLE SIZE (g)	TYPICAL EXTRACT VOLUME (ml)
0.5 - 5	1 - 10

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

INTERFERENCES: Any electron capturing species in the retention time region of trichlorobiphenyl isomers through octachlorobiphenyl 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.

TYPICAL SURROGATES	TYPICAL RECOVERIES (%)
pentachlorobenzene	50 - 120
2,4,6-trichloro-biphenyl	50 - 120
3,3',4,4'-CL4-biphenyl-d6	50 - 120

APPARATUS AND MATERIALS:
Burdick and Jackson hexane for sample extraction
Concentrated hydrochloric acid for reduction of the nitro group.
Mossy tin for catalytic reduction of the nitro group.
Concentrated sulfuric acid for 50% extract rinse.
Distilled deionized water for dilution of hydrochloric and sulfuric acids
Sodium hydroxide pellets for freeing the amine salt.
Silica gel columns impregnated with potassium permanganate, sulfuric acid, and potassium hydroxide.
Disposable glassware.
Nitrogen for extract volume reduction.
(See flow sheet for this extraction method in PCFS06.)

LIMITATIONS: Method applies only to matrices which contain hydrolizable electron capturing species in the trichlorobiphenyl through octa-chlorobiphenyl isomer retention time region for EC detection methods.

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

DATES OF METHOD CREATION AND UPDATES: 4/24/84

FLOW SHEET PCFS06

FOR ESC EXTRACTION METHOD PCEX06

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

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

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

WEIGH OUT SAMPLE INTO A 40 mL VIAL [ ] WEIGHT SAMPLE ----------

SURROGATE SPIKE OF SAMPLE ( ) SPIKE ----------

---------- ----------

ADD 1.5 g MOSSY TIN, AND 6 mL CONC. HCl TO SAMPLE [ ]
ALLOW TO STAND OVERNIGHT

RINSE COLUMN WITH 2 X 20 mL [ ] HEXANE

ADD 15 mL WATER TO SAMPLE AND BASIFY WITH NaOH (4-5g) [ ]

CLEAN-UP COLUMN DESCRIPTION
25 mL DISPO PIPET

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

RINSE EXTRACT 1 X 10 mL 50% SULFURIC ACID [ ]

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

ELUTE WITH 30 mL HEXANE [ ]

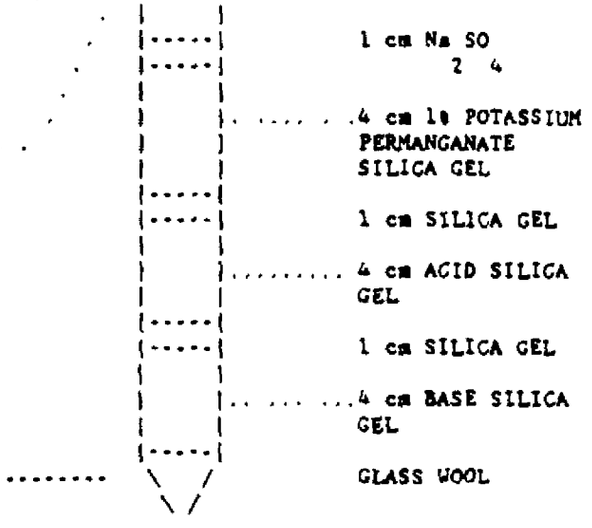
NITROGEN BLOW DOWN TO 1 mL [ ]

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

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

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

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



MQMS 221132

ESC Standard Extraction Method (SEM) TITLE. PCBs in Oil Matrices Requiring Cleanup

ESC Standard Extraction Method No PCEX30

MATRI(X),(CES):	TYPICAL SAMPLE SIZE (g)	TYPICAL EXTRACT VOLUME (ml)
Oils, that contain acid or base hydrolizable impurities	0.5 - 5	1 - 10

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

INTERFERENCES: Any electron capturing species in the retention time region of trichlorobiphenyl isomers through octachlorobiphenyl isomers for ECAN05
Any species in the appropriate rentention time region which give the same relative characteristic mass responses as PCB isomers for MSAN25.

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 benzene for sample extraction.
Burdick and Jackson hexane for column elution.
Silica gel columns impregnated with potassium permanganate, sulfuric acid, and potassium hydroxide.
Disposable glassware.
(See flow sheet for this extraction method in PCFS07.)

LIMITATIONS: Method applies only to matrices contain hydrolizable impurities that the cleanup column can remove. EC SAMs are valid for CL3-BP through CL10BP. 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: 10/19/87

FLOW SHEET PCFS30

FOR ESC EXTRACTION METHOD PCEX30

SAMPLE ID: ..... MRC EXTRACT # .....

..... LOG NO: .....

EXTRACTION DATE and TIME: .....

PIPET 1 mL

WEIGH OUT SAMPLE INTO A 14 mL VIAL [ ] WEIGHT SAMPLE (1 g) .....

SURROGATE SPIKE OF SAMPLE [ ] SPIKE .....

.....

ADD 10 mL BENZENE TO VIAL [ ]

RINSE COLUMN WITH 2 X 20 mL

[ ] HEXANE

SHAKE UNTIL OIL IS INTO SOLUTION [ ]

CLEAN-UP COLUMN DESCRIPTION 25 mL DISPO PIPET

PLACE 1 mL EXTRACT ONTO HEAD OF COLUMN [ ]

1 cm Na_2SO_4

ELUTE COLUME WITH 40 mL HEXANE [ ]

4 cm 1% POTASSIUM PERMANCANATE SILICA GEL

1 cm SILICA GEL

COLECT COLUMN ELUENT IN A 50 mL CENTRIFUGE TUBE [ ]

4 cm ACID SILICA GEL

NITROGEN BLOW DOWN TO 1 mL [ ]

1 cm SILICA GEL

4 cm BASE SILICA GEL

EXTRACT NO: .....

DATE/TIME COMPLETED ...../.....

GLASS WOOL

ANALYST: .....

ESC JOB NO: .....

MONS 221134

Appendix B. Brief Description of Analysis Approaches Used in the Analysis of Incidental PCBs.

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

B. Mason Hughes and David E. McKenzie
Environmental Sciences Center
Monsanto Company
800 N. Lindbergh Blvd.
St. Louis, Mo. 63167

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 implements this instrumental method for the analysis of PCBs in various types of samples.

(continued)

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 quantities of PCB congeners are determined by comparing the PCB congener responses in the sample of interest with PCB congener 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 divided into two types of CGC/MS analyses. The first is for products and waste streams which contain major components which can be chromatographically resolved from CL1-biphenyl through CL10-biphenyl congeners, when the product or waste stream components are present at concentrations ten million times those 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 be compared to standard PCB congener areas.

The second type of analysis applies to Monsanto products and waste streams which contain major components which cannot be chromatographically resolved from PCB congeners and for all air emission and water effluent samples. This second type of analysis involves first isolation of all PCB congeners which are present in a representative sample into a suitable solvent. This extracting solvent can then be analyzed for PCB congeners as above in the first type of analysis, since the extracting solvent is chosen to be chromatographically resolved from the PCB congeners of interest. 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 CGC/MS 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 are obtained and validated for the presence or absence of PCB congeners in various Monsanto materials.

<u>Extraction of products, waste streams, air emissions and water effluents:</u>

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 property differences between PCBs and major compounds in various samples 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 isolation. However it is important to demonstrate that, during this isolation phase, PCB congeners have not been removed during the extraction. This is done in two ways. The first way involves the use of surrogate compounds which act exactly like PCB congeners, yet are mass spectrometrically different. This is normally accomplished by using 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 congeners detected. However extraction of all PCB congener classes can be demonstrated

(continued)

only if one has isotopically labelled PCB congeners for each congener class Since at this time there are no good sources of high purity surrogates 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 of 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.

<u>GGC/MS analysis of extracts, products and waste streams:</u>

As mentioned above, sample extracts, products and waste streams can be injected directly into the GGC/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 GGC/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.

The 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 interferences. This is done in order to show that the GGC/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.

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Quantitation and Identification of PCB Congeners:

Tables 1 and 2 show how the 209 PCB congeners are distributed amoung 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. To insure that the proper retention time region is being monitored for the proper chlorine class, a PCB window standard is also analyzed under the same conditions as the samples are analyzed. This window standard contains the first and last eluting PCB congener in each of the chlorine classes. Analysis of this standard documents that all possible congeners of each chlorine class can be detected using the mass spectrometer scan parameters chosen for the analysis Therefore the analysis conditions can detect all of the 209 PCB congeners.

PCB congeners are qualitatively identified from the ratio of the peak areas of the two molecular ion chromatograms. If the ratio of characteristic and confirming ion chromatographic peaks are within 30% of the experimental ratio obtained from the corresponding chlorine class in the PCB congener standard analysis, and the two peaks maximize within two mass spectrometer scans, then the concentrations of PCB congeners are calculated from these ion areas and appropriate dilution factors. If the peak area ratio does not agree within 30% of the experimental ratio for a particular PCB congener class, then this response is assumed not to be due to a PCB congener.

Summary:

The above appoach 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) must be used to validate that the data can be used for the certification of the absence of incidental PCBs in Monsento 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.

		PCB Congener Class (Number of Congeners)				
Characteristic Masses	Number of Chlorines	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)

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

Characteristic Masses	Number of Chlorines	PCB Congener Class (Number of Congeners)				
		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)

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Appendix C. Listing of Procedure Files and Examples of Computer outputs Produced from the Analysis of the System Performance Standard. (SYSPRF Transfer File.)

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