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PCB Congener Analysis of XAD-2 Resins and GFF Filters Using GC/ECD

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Standard Operating Procedure MSL-M-093-00

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1.0 Application and Scope

1.1 This SOP is applicable to the analysis of GFF filter and XAD-2 resin extracts prepared according to SOPs MSL-M-091 and MSL-M-092 for polychlorinated biphenyls (PCB) and trans-nonachlor by capillary gas chromatography with ^{63}Ni electron-capture detection.

1.2 This procedure provides typical gas chromatography (GC) conditions for the detection of trace levels of PCBs and trans-nonachlor, methods for identifying the analytes, and methods for analyte quantitation using the internal standard method. Attachment 1 lists the most frequently analyzed compounds. However, this list may be amended to meet requirements of specific projects.

2.0 Definitions

The following terms and acronyms may be associated with this procedure:

ECD	Electron capture detector or detection
GC	Gas chromatography
PCB	Polychlorinated biphenyl
RF	Response factor
RRF	Relative response factor; response factor of analyte normalized to the response factor of the internal standard.
RSD	Relative standard deviation (%)
RT	Retention time
IS	Internal standard - compound(s) added just prior to analysis on instrument.
Surrogate	Compound(s) added prior to extraction to assess efficiency of method.

In addition, it should be noted that the numbering scheme used for PCB congeners, e.g. PCB 3, is that used by Ballschmiter and Zell.

3.0 Responsible Staff

Project Manager: A Scientist responsible for 1) administration of the project; 2) providing project specific quality control requirements to the laboratory; 3) defending the data in a Quality Assurance Audit; and 4) reporting results to client.

Laboratory Supervisor: A Technical Specialist or Scientist having expertise in the principles involved with this procedure and in the use of the GC. Responsible for 1) ensuring that analysts are trained in operation of the GC; 2) appropriate quality control samples are included with the sample analysis to monitor precision and accuracy of the analysis; 3) checking the analysts' work to ensure that data are collected and interpreted correctly; 4) making decisions regarding problems with the analysis or deviations from the SOP; 5) defending the data in a Quality Assurance Audit; and 6) reporting results to project manager or client.

Analyst: A Technician, Technical Specialist, or Scientist assigned to conduct analyses using this procedure. Responsible for 1) understanding the proper use and maintenance of the GC; 2) recording information regarding instrument use and maintenance in the appropriate log books; 3) analyzing the appropriate number of quality assurance samples for each batch of samples analyzed; 4) tabulating all sample and QC data and reviewing the quality of the data based on QC guidelines presented in this SOP and any other project-specific QC guidelines; 5) reporting results to the Project Manager; and 6) defending the data during an audit.

Quality Assurance Representative: A qualified staff member assigned to the Quality Assurance Unit. Responsible for monitoring the project activities and conducting Quality Assurance Audits to ensure that 1) analysts have conducted the analysis according to the SOP and that deviations from the SOP have been noted in the appropriate log book or in the project files; 2) instrument use and maintenance records are kept correctly; and 3) data have been reported and presented accurately.

4.0 Procedures

The GC must be maintained and operated as described in Battelle SOP No. MSL-M-075.

4.1 GC Preparation

The primary quantitation GC column is a 60 meter x 0.25 mm (i.d.) fused silica capillary column coated with a 5% phenyl-, 95% methyl-polysiloxane film of 0.25 µm thickness. (J&W Scientific, Inc., 60 meter DB-5 or equivalent). The confirmation column is a 60 m x 0.25 mm (i.d.) fused silica capillary column coated with a 14% cyanopropylphenyl-86% methyl polysiloxane film of 0.25 m thickness (J&W Scientific, Inc. 60 meter DB-1701 or equivalent). Both columns are installed in a single splitless injection port using a 2-hole ferrule.

4.2 Sample Collection, Preservation, and Handling

To conduct this analysis, the analyst should receive the samples as solvent extracts reduced to an appropriate volume (as specified in SOP MSL-M-091 or MSL-M-092). Holding times to be followed are those specified in the project specific QAPjP; normally the holding time for extracts is 40 days from date of extraction. If holding times have been exceeded, the Project Manager should be notified immediately. Refer to project-specific plans or protocols for sample collection, preservation, and handling methods.

4.3 Sample Specifications

Sample preparation methods may vary depending on the sample matrix and project needs; refer to project-specific protocols. Normally, this method is used to analyze extracts prepared according to Battelle SOPs MSL-M-091 and MSL-M-092. Samples and standards for analysis using this SOP should be prepared in hexane.

Table 1: Suggested Instrument Conditions for PCB and Chlorinated Pesticide Analysis

Primary Column (DB-5) Conditions:

Injection port type	Splitless
Injection port temperature	250°C
Detector temperature	300°C
Initial temperature	50°C
Initial hold	1.5 min
Ramp 1 rate	10°C/min
Final temp 1	105°C
Final time 1	0.0 min
Ramp 2 rate	1°C/min
Final temp 2	225°C
Ramp 3 rate	10°C/min
Final temp 3	280°C
Final time 3	20 min
Carrier gas	Hydrogen
Carrier gas velocity	60 cm/sec
ECD make-up gas	Nitrogen
Make-up gas flow	30 cc/min
Split vent flow	215 cc/min
Split vent on-time	1.5 min
Injection volume	5 µL
Injection speed	10 µL/sec
Hot needle time	0.07 min
Needle residence time	0.2 min

4.4 Analyte Identification

Prior to sample analysis, the elution order of the analytes of interest must be determined by analyzing the analytes individually or in combination with other analytes having known or predetermined retention times. The retention times of the analytes have all been verified on both the quantitation (DB-5) and confirmation columns (DB-1701) specified above under the GC conditions listed in Table 1, and are listed in Attachments 1 and 2. The elution order of the congeners was determined from data provided by another laboratory using similar GC conditions (Mullins et al. 1985, 1994 personal communications). Additional information on analyte identification is discussed in Section 4.6.1.

4.5 Instrument Calibration

Before the sample is injected into the GC, the detectors must be calibrated to determine the response of the detector to the analytes of interest. Demonstration of linearity of detector response is required before sample analysis. Calibration checks must be analyzed at a minimum frequency of once every 10 samples during sample analysis.

4.5.1 *Initial Calibration:* Prior to initiating any sample analyses initial calibration is performed by analyzing calibration standards at a total of seven levels spanning the concentration range of 9.1 ng to 1830 ng as ?Total PCBs". Not all the congeners respond or are clearly resolved from other congeners at all these levels. On the DB-5 quantitation column, eleven congeners (BZ #s 12, 13, 100, 147 & 124, 134, 130, 129, 167, 173, and 189) are only determinable at three of these concentration levels. The calibration curves for these consist of the three concentrations plus zero. All other congeners are calibrated using a minimum of four concentrations. Calibration standards include the appropriate surrogates (Surr.) and internal standards (IS) at concentrations identical to their concentrations in the samples (see MSL-M-091 and MSL-M-092). An initial calibration must also be run if any GC conditions have changed significantly or if continuing calibration acceptance criteria (CCAC) are not met. Initial calibration acceptance criteria are a correlation coefficient (r^2) of 0.95 for a minimum 4 point curve using a quadratic or linear fit.

4.5.2 *Continuing Calibration (CCAC):* A mid-level calibration solution is analyzed as a calibration check minimally every 10 samples while samples are being analyzed. All sample analyses must be bracketed by two calibration check standards that meet calibration criteria. Continuing calibration acceptance criteria for the primary quantitation column are a 75-125% recovery relative to the total PCB value expected.

4.5.2.1 *Performance Criteria*: Additional performance criteria that will be evaluated within each CCAC include: a recovery of 50-150% for PCBs 6 & 205 (which represent small peaks), and a recovery of 75-125% for PCBs 101, 185, 44, & 180 (which represent average and large peaks). To ensure proper identification, the retention time of the internal standard reference peaks, PCB 30 and PCB 204, cannot shift by more than ±0.4 min (see Section 4.6.1).

4.5.2.2 *Internal Standard Criteria:* To ensure that the internal standards are not interfered with the area or height ratios between the internal standards PCB 30 and PCB 204 in the samples are monitored. If the area or height ratios observed in the samples differ from those observed during initial calibration by more than ±15% relative percent difference (RPD), all congeners must be quantitated relative to the uncontaminated internal standard and the data flagged accordingly.

4.6 Sample Analysis Procedure

Samples are analyzed under the same analytical conditions as the calibration standards. Samples must be bracketed by acceptable calibrations (see acceptance criteria in Section 4.5.2). Criteria for accepting peaks as analytes of interest are explained in Sections 4.6.1 through 4.6.4.

4.6.1 *Retention Time Windows:* Analytes are identified by the data system by setting allowable time windows for reference peak and analyte peak retention times. Initial retention times are set during the initial calibration of the instrument. From that point forward, the system utilizes retention time windows in which to "look" for peaks of interest and reference peaks. The reference peak windows are set at ±0.4 min. and the analyte peak windows are set at ±0.10 min. Since the internal standard reference peaks are large and clearly resolved using a larger window for recognizing them is justified. The data system then uses the actual retention time of the internal standard reference peaks to adjust the position of the analyte peak windows, which are much narrower, to compensate for any minor chromatographic drift. One internal standard reference peak shall also be designated an RRT reference peak to further assist in proper peak identification through the use of relative retention times.

4.6.2 *Second Column Confirmation*. Since each injection is split between the quantitation column (DB-5) and confirmation column (DB-1701) all sample results will be confirmed by whether or not a peak is observed at the appropriate retention time on both columns. The retention time criteria described in Section 4.6.1 apply to the confirmation column also. Trans-nonachlor can only be quantitated on the DB-1701 since it is interfered with by PCB 99 on the DB-5. As a result of this, second column confirmation of trans-nonachlor is not possible except as PCB 99 and trans-nonachlor on the DB-5. When trans-nonachlor is confirmed in this manner the PCB 99 value must be flagged accordingly.

4.6.3 *Resolution.* Resolution on the primary (DB-5) column should be sufficient to separate congeners #17 and #18 into two peaks with a valley less than half the height of PCB #17. If this cannot be accomplished a new column must be installed or the instrument conditions optimized further.

4.6.4 *Minimum Area or Height*: Peaks with a signal-to-noise ratio of three or less should be regarded as not detected unless otherwise noted in a specific project plan and/or documented by project management.

5.0 Data Analysis and Reporting

5.1 Data Recording

Data quantitation and calculations will be performed on personal computers using commercial software such as Varian Star Chromatography Software (Version 4.0 or higher), Microsoft Excel (Version 4.0 or higher) or database software (Access Version 2.0). All transfers of data to forms and data reductions (e.g., concentration calculations, means, standard deviations) will be checked by the analyst and approved by the Laboratory Supervisor. Hard copies of GC printouts of calibrations and sample data and spreadsheet reports will be kept in the GC/ECD files. A copy of the summary sheets and extraction logs will be placed in the appropriate project file in the Chemistry Group Central Files. Hard copies of chromatograms from each sample and all calibrations will be kept in the GC/ECD files unless otherwise noted in a specific project plan. All GC data files will be archived on magnetic tape.

5.2 Sample Quantitation

The internal standard method is used for quantitation. PCB 30 is used to quantify all PCB congeners with retention times up to and including PCB 110, all other congeners are quantitated vs. PCB 204. PCB 30 is used to quantitate the surrogates PCB 14 and PCB 65 and PCB 204 is used to quantitate the surrogate PCB 166. In addition, the results reported are corrected for the recovery of the surrogates PCB 65 and PCB 166; the surrogate PCB 14 is not used because it is oftentimes interfered with. The recovery of PCB 65 is used to correct the congeners quantitated vs.

PCB 30 and the recovery of PCB 166 is used to correct the congeners quantitated vs. PCB 204. If the ratio of internal standard areas exceeds the criteria set in Section 4.5.2.2, all congeners must be quantitated relative to the uncontaminated internal standard and the data must be flagged accordingly.

The concentration of a specific analyte in a sample is calculated by the Varian Star chromatography workstation. The system uses the concentration amounts for the individual analytes entered into the peak table and the results from the calibration standards to generate the coefficients of a polynomial curve fit that is, in turn, used to calculate the analytical concentrations. This result is then adjusted for internal standard and surrogate recoveries in an Excel spreadsheet:

$Star\ result = Amt_{(star)}$

Where:

$Amt_{(star)}$ *is obtained by solving:*

$Area(or\ height)_{(unk)} = A * (Amt_{(star)}{}^2 + B * Amt_{(star)} + C)$

Where:

A, B & C = coefficients of the polynomial equation
$Amt_{(star)}$ *= amount of compound present in extract unadjusted for internal or surrogate stds*
$Area(or\ height)_{(unk)}$ *= area or height of the peak for the selected compound found in the analysis run.*

At this point the result is not corrected by any internal standards. The results are then imported to an Excel spreadsheet using various star macros and adjusted for internal and surrogate standard recoveries.

$Result = Amt_{(ca)} / (Sample\ Volume)$

Where:

$Rec_{(istd)} = Amt_{(istd)} / Amt\ expected_{(istd)}$
$Rec_{(surr)} = Amt_{(surr)} /Amt\ expected_{(surr)})/Rec_{(istd)}$
$Amt_{(adj)} = Amt_{(star)} /Rec_{(istd)}$
$Amt_{(ca)} = Amt_{(adj)} /Rec_{(surr)}$

Where:

$Amt_{(ca)}$ *= Amount of compound present in analysis run*
$Amt_{(istd)}$ *= Amount of internal standard present in extract, calculated by Varian Star*
$Amt\ expected_{(istd)}$ *= Amount of internal standard added to extract*
$Amt_{(surr)}$ *= Amount of surrogate standard present in extract, calculated by Varian Star*
$Amt\ expected_{(surr)}$ *= Amount of surrogate standard added to extract*

5.3 Confirmation Data

The identification of particular PCB congeners is confirmed in all the samples by analysis on a column of dissimilar polarity (DB-1701). Confirmation is strictly by retention time only. The same criteria for retention time windows as described for the quantitation column (Section 4.6.1) are applied to the confirmation column.

5.4 Surrogate and Spike Recovery Calculation

Surrogate and Spike recoveries are calculated from the quantitation column. Calculations are as follows:

$$\text{Surrogate \% Recovery} = \frac{Q_d}{Q_a} \times 100$$

Q_d = *Quantity determined by analysis*
Q_a = *Quantity added*

$$\text{Matrix Spike Recovery} = \frac{(SSR-SR)}{ESR} \times 100$$

SSR = Spike sample result
SR = Sample result
ESR = Expected sample result = Q_a*/Divisor, where Divisor = amount sample analyzed*
The relative percent difference (RPD) between replicates is calculated as follows:

$$RPD = \frac{|SR - SDR|}{1/2\,(SR + SDR)} \times 100$$

SDR = Sample Duplicate Result

6.0 Quality Control

Some quality control considerations associated with this SOP are described in the individual sections to which they apply. The following additional quality control criteria apply unless otherwise specified in a project specific QAPjP:

Field and Method Blanks	≤10 ng Total PCB
Surrogate Recoveries	40-140% (excluding PCB 14)
Matrix Spike Recoveries	50 to 150% Total PCB & 70% of analytes within 50-150% range
Blank Spike Recoveries	70-130% Total PCB, & 70% of analytes within 60-140% range
Sample Duplicate RPD	≤50% Total PCB and ≤100% for analytes ≥5X MDL

7.0 Safety

All analysts following this procedure should be aware of routine laboratory safety concerns, including the following:

1. Protective clothing and eyeglasses should be worn when appropriate
2. Proper care must be exercised when using syringes
3. Certain areas of the GC system are heated. Avoid bodily contact with these areas and use care in handling flammable solvents in and around the GC system.

8.0 Training

All analysts following this procedure will be directly supervised by the Principal Investigator, qualified analyst, or laboratory supervisor until they have demonstrated to the satisfaction of the supervisor that they are capable of operating the GC independently. At a minimum, the analyst trainee should be competent in operation and maintenance of the GC (SOP No. MSL-M-075). The analyst trainee should also be able to analyze and quantify a multi-point calibration and quantitate a sample of known concentration (e.g., a reference material or matrix spike) within established control limits. Documentation of training will be recorded on training assignment and on-the-job training forms from SOP MSL-A-006. Records of this training will be kept by the laboratory Quality Assurance Representative.

9.0 References

9.1 MSL-A-006 Marine Sciences Laboratory Training.

9.2 MSL-M-075 Routine GC Maintenance.

9.3 MSL-M-091 Extraction and Cleanup of Resin Cartridges for Polychlorinated Biphenyls and trans Nonachalor.

9.4 MSL-M-092 Extraction and Cleanup of Glass Fiber Filters for Polychlorinated Biphenyls and Nonachlor.

9.5 Quality Assurance Plan Green Bay Mass Balance Study "Cleaning Methods for XAD-2 Resin and Filters," U.S. Environmental Protection Agency (EPA). 1986.

9.6 Analytical Quality Assurance Project Plan (QAPjP) for the EPA Lake Michigan PCB Mass Balance Study, DRAFT, dated October 25, 1994.

9.7 K Ballschmiter and Zell, "Analysis of Polychlorinated Biphenyls by Capillary Gas chromatography," Fresenius Z. Analytical Chemistry, #302 pp. 20-31 (1980)

Attachment 1: Mixed Congener Standard on DB-5
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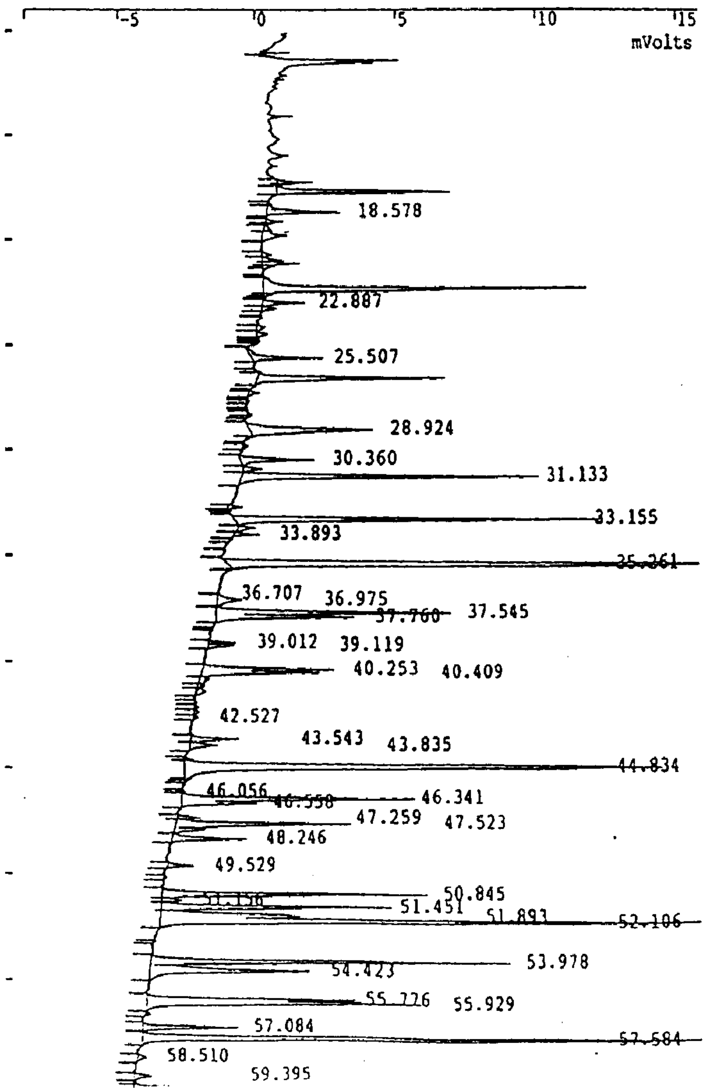
```
Title       : 7 pt pp-376 GLNPO june using height for cal
Run File    : C:\STAR\MODULE16\728JN4\7284013.RUN
Method File : C:\STAR\MODULE16\728JN4\7284014.MTH
Sample ID   : PP-376C 183

Injection Date: 26-MAY-95 4:51 PM    Calculation Date: 22-JUN-95 2:56 PM

Operator    : TJF                    Detector Type: ADCB (10 Volts)
Workstation:                         Bus Address  : 16
Instrument : Varian Star #1          Sample Rate  : 5.00 Hz
Channel     : A = 5                  Run Time     : 152.503 min

*********** Star Chromatography Software ********** Version 4.01 *************

Chart Speed =    0.39 cm/min   Attenuation = 10          Zero Offset = 35%
Start Time  =   10.000  min     End Time    = 128.000 min  Min / Tick  = 5.00
```



Attachment 1: Mixed Congener Standard on DB-5
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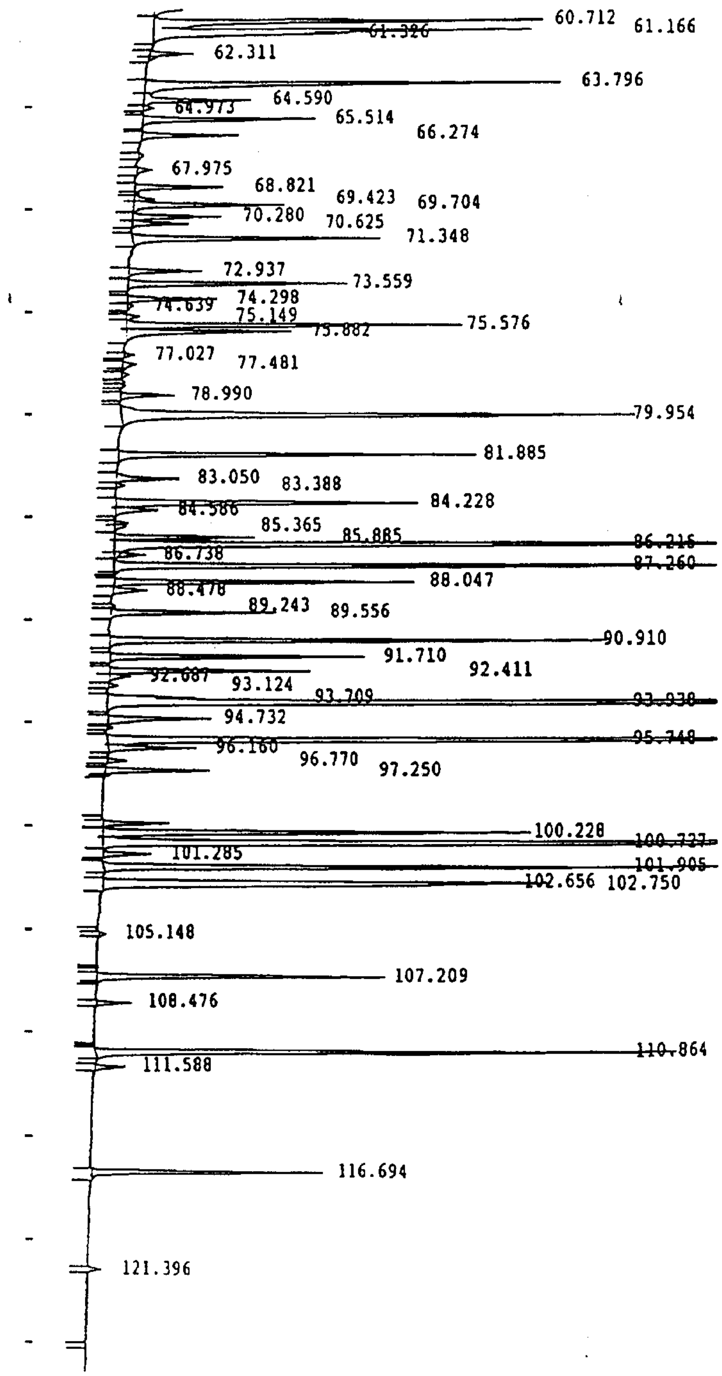

Attachment 1: Mixed Congener Standard on DB-5

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```
Title       : 7 pt pp-376 GLNPO june using height for cal
Run File    : C:\STAR\MODULE16\728JN4\7284013.RUN
Method File : C:\STAR\MODULE16\728JN4\7284014.MTH
Sample ID   : PP-376C 183

Injection Date: 26-MAY-95 4:51 PM    Calculation Date: 22-JUN-95 2:56 PM

Operator    : TJF                    Detector Type: ADCB (10 Volts)
Workstation:                         Bus Address  : 16
Instrument  : Varian Star #1         Sample Rate  : 5.00 Hz
Channel     : A = 5                  Run Time     : 152.503 min

*********** Star Chromatography Software ********** Version 4.01 **************

Run Mode         : Analysis
Peak Measurement: Peak Height
Calculation Type: External Standard
```

Peak No.	Peak Name	Result (NG/L)	Ret. Time (min)	Time Offset (min)	Height (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1	1	12.452705	18.578	0.006	264	VB	6.2	
2	3	7.748489	22.887	0.005	154	BV	6.1	
3	4+10	3.673396	25.507	0.009	257	BB	6.6	
4	7+9	1.111898	28.924	0.030	437	BB	11.9	
5	6	1.810442	30.360	0.010	269	BB	7.5	
6	8+5	14.648691	31.133	0.006	1047	BB	7.3	
7	14(SURR)	19.450569	33.155	0.001	1303	BB	7.4	
8	19	0.278382	33.893	0.003	92	BB	6.3	
9	30(ISTD)	10.014711	35.261	0.041	3154	BB	7.3	R
10	12	0.075297	36.707	0.033	12	BV	1.8	
11	13	0.178523	36.975	-0.013	92	VB	10.1	
12	18	3.918240	37.545	0.007	831	BV	7.0	
13	15+17	3.817946	37.760	0.008	501	VB	7.8	
14	24	0.052955	39.012	0.005	100	BV	7.1	
15	27	0.200533	39.119	-0.011	94	VB	8.5	
16	16	2.078020	40.253	0.005	478	BV	7.3	
17	32	2.000064	40.409	0.008	430	VB	8.7	
18	29	0.051388	42.527	0.000	16	VB	5.6	
19	26	0.683344	43.543	0.019	174	BV	7.4	
20	25	0.299107	43.835	0.014	99	VB	8.1	
21	31+28	10.189798	44.834	0.014	1700	VB	12.0	
22	21	0.031160	46.056	0.023	10	BV	9.7	
23	33	3.577584	46.341	0.021	829	VV	7.8	
24	53	0.672404	46.558	0.002	272	VB	9.7	
25	51	0.179196	47.259	-0.000	82	BV	6.9	
26	22	2.948125	47.523	0.020	637	VV	7.8	
27	45	0.937357	48.246	0.009	272	VB	6.8	
28	46	0.377848	49.529	0.004	95	BB	6.5	
29	52	4.857748	50.845	0.008	941	BV	7.5	
30	43	0.266150	51.156	0.001	73	VV	8.0	
31	49	2.580539	51.451	0.012	828	VV	7.4	
32	48+47	1.112766	51.893	0.006	505	VV	0.0	
33	65(SURR)	4.909873	52.106	0.003	2146	VB	7.5	
34	44	4.793020	53.978	0.013	1277	BV	7.7	
35	42+37	1.452151	54.423	0.009	580	VB	9.1	
36	41+71	2.459767	55.776	0.009	751	BV	8.2	
37	64	1.899905	55.929	0.012	974	VB	10.2	
38	40	0.956243	57.084	0.004	345	BV	7.5	

Attachment 1: Mixed Congener Standard on DB-5

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39	103(ISTD)	9.980792	57.584	0.039	2275	VB	7.6	R
40	100	0.102683	58.510	0.003	33	BB	9.2	
41	63	0.205672	59.395	0.015	68	BV	8.2	
42	74	2.026874	59.972	0.021	767	VV	7.7	
43	70+76	3.643651	60.712	0.018	1401	VV	8.0	
44	66	5.537148	61.166	0.017	1361	VV	9.2	
45	95	2.298095	61.326	-0.000	719	VB	11.5	
46	91	0.537131	62.311	0.005	164	BV	7.2	
47	56+60	3.821698	63.796	0.023	1497	BV	8.2	
48	92+84	1.896827	64.590	0.004	391	VV	7.7	
49	89	0.109377	64.973	0.012	43	VB	6.5	
50	101	1.932718	65.514	0.007	625	BB	8.0	
51	99	0.758792	66.274	0.008	358	BB	7.6	
52	83	0.143149	67.975	0.004	57	BB	7.6	
53	97	0.568289	68.821	0.006	327	BV	7.9	
54	81	0.184326	69.423	0.010	81	VV	7.9	
55	87	1.073545	69.704	0.013	551	VV	8.3	
56	85	0.709927	70.280	0.005	328	VV	8.0	
57	136	0.778711	70.625	0.005	210	VB	7.4	
58	110+77	2.019769	71.348	0.013	911	BB	8.4	
59	82	0.469813	72.937	0.006	273	BB	7.5	
60	151	1.803968	73.559	0.008	801	BB	8.0	
61	135+144	0.948432	74.298	-0.000	333	BV	8.1	
62	147+124	0.395914	74.639	0.028	23	VB	7.6	
63	107	0.124099	75.149	0.013	51	BV	7.6	
64	123+149	3.043263	75.576	0.008	1224	VV	8.1	
65	118	1.255572	75.882	0.020	597	VB	8.3	
66	134	0.068224	77.027	0.006	40	BB	6.4	
67	114+131	0.141561	77.481	0.020	55	BV	8.3	
68	146	0.400207	78.990	0.016	204	BB	7.8	
69	132+153+105	4.593065	79.954	0.013	1858	BB	9.5	
70	141	1.841368	81.885	0.009	1285	BB	8.1	
71	137+176	0.271340	83.050	0.005	236	BV	7.9	
72	130	0.071601	83.388	0.015	33	VB	7.7	
73	163+138	2.926401	84.228	0.009	1103	BV	10.6	
74	158	0.252452	84.586	0.010	160	VB	8.8	
75	129	0.015677	85.365	-0.003	43	VP	17.4	
76	178	1.193907	85.885	0.006	518	PV	8.1	
77	166(SURR)	4.808515	86.215	0.000	3252	VV	8.4	
78	175	0.194360	86.738	0.002	100	TS	0.0	
79	187+182	4.078599	87.260	0.001	2366	VB	8.4	
80	183	1.905587	88.047	0.002	1101	BV	8.1	
81	128	0.094070	88.478	0.023	126	VB	9.5	
82	167	0.041623	89.243	0.014	15	BV	6.6	
83	185	0.494288	89.556	0.007	605	VB	8.0	
84	174	3.529921	90.910	-0.001	1802	BB	8.6	
85	177	1.909970	91.710	0.005	934	BB	8.0	
86	202+171	0.871405	92.411	0.005	731	BV	8.0	
87	156	0.065165	92.687	0.011	82	VB	8.2	
88	173	0.034467	93.124	-0.000	35	BB	7.0	
89	157+200	0.439246	93.709	-0.002	326	BV	8.4	
90	204(ISTD)	9.931970	93.938	0.050	5983	VB	8.3	R
91	172+197	0.595701	94.732	0.004	385	BB	8.2	
92	180	6.918325	95.748	0.012	4264	BV	8.5	
93	193	0.444705	96.160	0.003	323	VB	8.4	
94	191	0.110430	96.770	0.002	70	BB	6.9	
95	199	0.430443	97.250	-0.007	388	BB	8.1	
96	170+190	1.942022	100.228	0.006	1556	BV	9.1	
97	DBC(SURR)	10.149161	100.727	-0.013	5274	VB	8.4	
98	198	0.125405	101.285	-0.002	179	TS	0.0	

Attachment 1: Mixed Congener Standard on DB-5
(Page 5 of 5)

99	201	4.806856	101.905	-0.002	2272	BB	8.3
100	203	2.407035	102.656	-0.012	1611	BV	8.3
101	196	1.977705	102.750	-0.013	1323	VB	10.8
102	189	0.039184	105.148	-0.020	26	BB	8.1
103	208+195	0.896954	107.209	0.005	1064	BB	7.9
104	207	0.093248	108.476	-0.015	133	BB	7.4
105	194	2.084478	110.864	-0.002	2088	PB	8.2
106	205	0.112808	111.588	-0.003	112	BB	7.7
107	206	0.777460	116.694	-0.007	849	BB	7.9
108	209	0.013712	121.396	0.000	48	BB	7.2
	Totals:	249.217190		0.826	82548		

Status Codes:
R - Reference peak

Total Unidentified Counts : 5777 counts

Detected Peaks: 196 Rejected Peaks: 0 Identified Peaks: 108

Amount Standard: N/A Multiplier: 1.000000 Divisor: 1.000000

Baseline Offset: -11 microVolts

Noise (used): 140 microVolts - monitored before this run

Rack: 1 Vial: 12 Injection Number: 1 Injection Volume: 5.0 ul

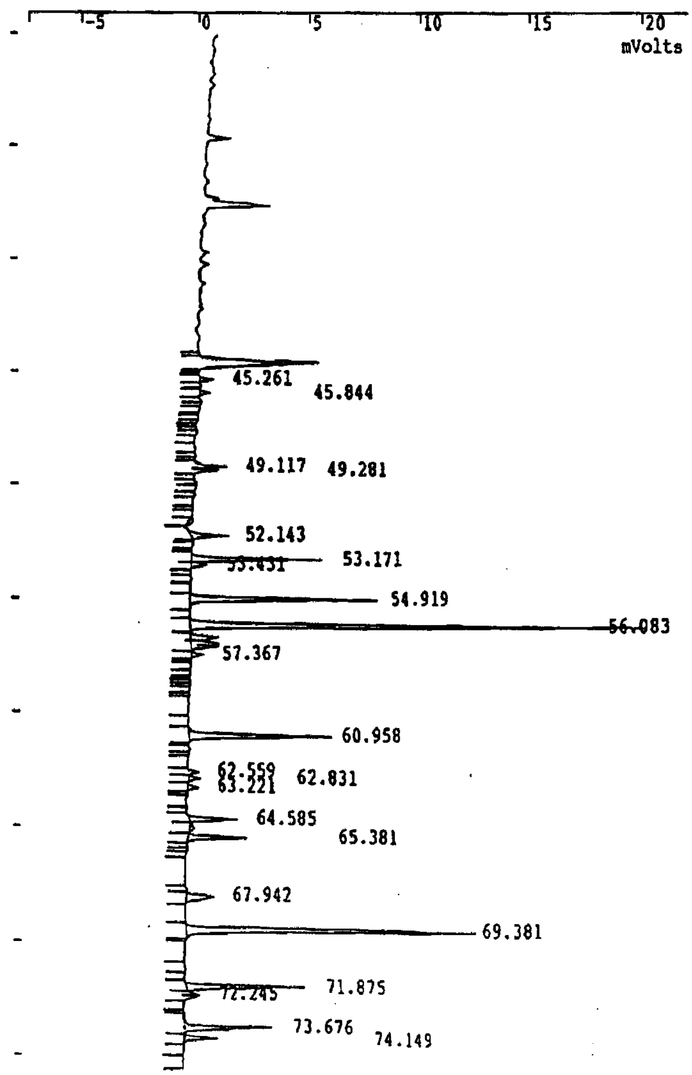
Original Notes:

MULLIN CAL STD W SINGLE LEVEL SURROGATES FOR SURROGATE
INTERNAL STD CALIBRATION

Appended Notes:

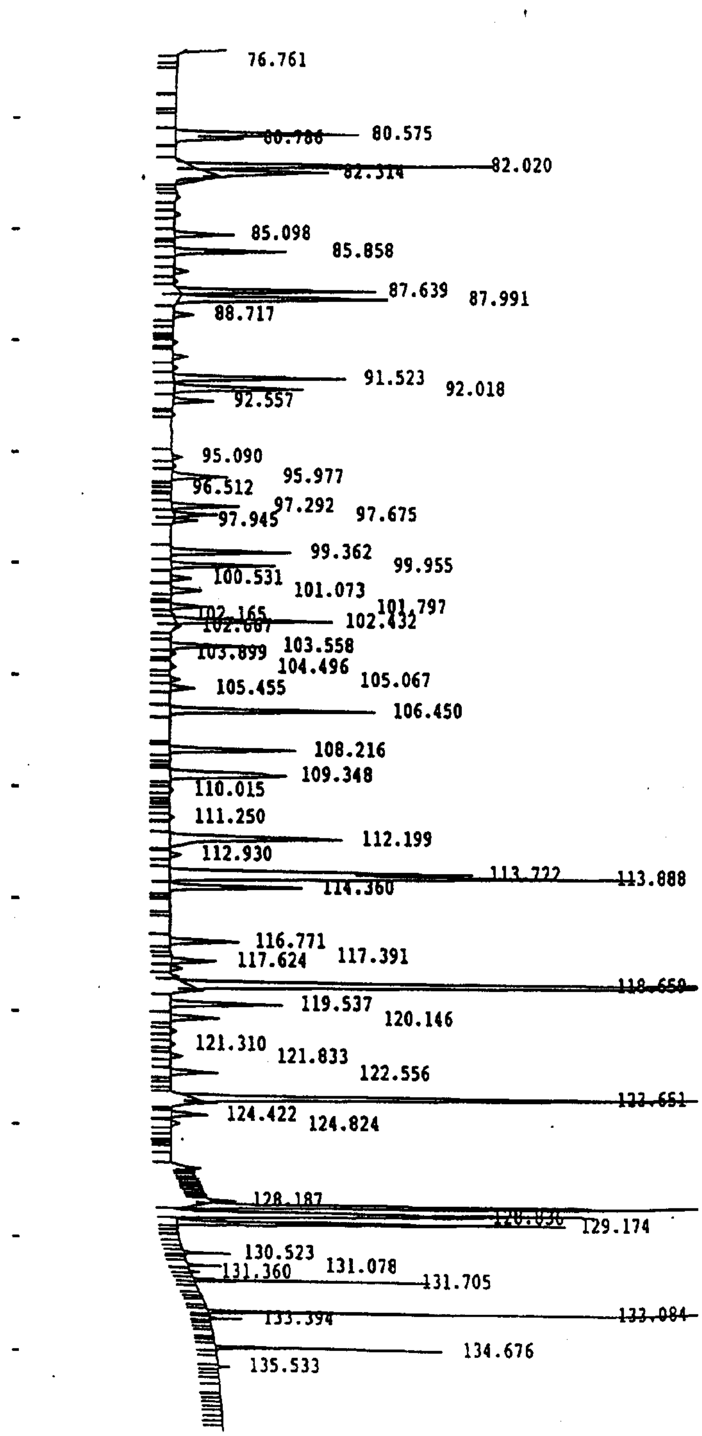
Attachment 2. Mixed Congener Standard on DB-1701
(Page 1 of 5)

```
Title       : june cal DB-1701 5 ul inj using height for cal
Run File    : C:\STAR\MODULE16\728JN4\7284013.RUN
Method File : C:\STAR\MODULE16\728JN4\7284014.MTH
Sample ID   : PP-376C 1B3

Injection Date: 26-MAY-95 4:51 PM    Calculation Date: 22-JUN-95 3:05 PM

Operator    : TJF                    Detector Type: ADCB (10 Volts)
Workstation:                         Bus Address  : 16
Instrument : Varian Star #1          Sample Rate  : 5.00 Hz
Channel     : B = 01                 Run Time     : 152.503 min

*********** Star Chromatography Software ********* Version 4.01 *************

Chart Speed =   0.42 cm/min   Attenuation = 12          Zero Offset = 25%
Start Time  =   30.000  min    End Time    = 140.000 min  Min / Tick  = 5.00
```



Attachment 2: Mixed Congener Standard on DB-1701

(Page 2 of 5)



Attachment 2: Mixed Congener Standard on DB-1701
(Page 3 of 5)

```
Title        : june cal DB-1701 5 ul inj using height for cal
Run File     : C:\STAR\MODULE16\728JN4\7284013.RUN
Method File  : C:\STAR\MODULE16\728JN4\7284014.MTH
Sample ID    : PP-376C 183

Injection Date: 26-MAY-95 4:51 PM    Calculation Date: 22-JUN-95 3:05 PM

Operator    : TJF                    Detector Type: ADCB (10 Volts)
Workstation:                         Bus Address  : 16
Instrument  : Varian Star #1         Sample Rate  : 5.00 Hz
Channel     : B = 01                 Run Time     : 152.503 min

*********** Star Chromatography Software ********** Version 4.01 **************

Run Mode          : Analysis
Peak Measurement: Peak Height
Calculation Type: External Standard
```

Peak No.	Peak Name	Result (NG/L)	Ret. Time (min)	Time Offset (min)	Height (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1	10	0.176037	45.261	0.000	65	BB	6.2	
2	4	3.018902	45.844	0.014	50	BB	6.1	
3	7	0.265841	49.117	0.018	95	BB	7.8	
4	9	0.335552	49.281	0.010	57	BB	9.7	
5	6	1.816117	52.143	0.011	174	BB	6.8	
6	8	14.159795	53.171	0.005	593	BV	7.3	
7	5	0.278926	53.431	-0.002	77	VB	7.2	
8	14SURR	5.036743	54.919	0.005	841	BB	7.5	
9	30ISTD	10.156128	56.083	0.039	2043	BP	7.2	R
10	19	0.281359	57.367	0.004	59	BB	7.2	
11	12+13+17+18	6.391715	60.958	0.010	643	BB	8.7	
12	24	0.052619	62.559	0.017	49	BB	7.0	
13	15	1.490831	62.831	0.014	54	BB	8.2	
14	27	0.203341	63.221	0.006	51	BB	7.3	
15	32	1.854917	64.585	0.004	223	BB	7.5	
16	16+29	2.099022	65.381	0.011	273	BB	7.6	
17	26+25	1.021916	67.942	0.008	128	BB	13.1	
18	28+31	10.125882	69.381	0.022	1314	BB	9.0	
19	21+33+53	4.102441	71.875	0.018	542	BB	8.1	
20	51	0.023595	72.245	-0.019	10	BB	11.4	
21	22	2.925104	73.676	0.015	402	BB	7.8	
22	45	0.928908	74.149	0.016	156	BB	7.6	
23	43+46+52	4.576473	76.102	0.011	476	BB	8.1	
24	65+47+49	3.705014	76.477	0.004	1378	BB	9.5	
25	48	0.847172	76.761	0.003	172	BB	8.0	
26	44	4.734031	80.575	0.016	803	BV	8.2	
27	42	1.447829	80.786	0.009	296	VB	9.7	
28	103ISTD	9.717182	82.020	-0.002	1354	BB	7.7	
29	41+71+100+64	3.625286	82.314	0.016	534	BB	11.7	
30	40+63	1.256547	85.098	0.004	260	BB	7.5	
31	74	2.065444	85.858	0.014	494	BB	7.9	
32	70	3.283874	87.639	0.017	864	BB	8.0	
33	66+95	5.817988	87.991	0.017	911	BB	9.9	
34	91	0.533801	88.717	0.009	90	BB	7.7	
35	60+101	5.634208	91.523	0.005	760	BB	8.2	
36	56+99	3.559681	92.018	0.014	572	BB	9.8	
37	89+84	1.446028	92.557	0.001	174	BB	7.9	
38	83	0.158861	95.090	0.004	46	BB	8.1	

Attachment 2: Mixed Congener Standard on DB-1701
(Page 4 of 5)

39	92+97	1.070954	95.977	-0.002	245	BB	8.7	
40	trans nonach	0.006340	96.512	-0.013	2	BB	2.6	
41	87	1.052906	97.292	0.005	296	BB	7.8	
42	85	0.695014	97.675	0.004	187	BB	7.8	
43	136	0.726305	97.945	0.001	104	BB	7.9	
44	110	2.009048	99.362	0.009	530	BB	8.0	
45	151	1.796553	99.955	0.003	458	BB	7.6	
46	144	0.630569	100.531	0.002	92	BB	7.2	
47	77	0.228873	101.073	-0.003	133	BB	8.4	
48	82	0.464388	101.797	0.015	161	BB	7.6	
49	135	0.156599	102.165	0.014	10	BB	8.0	
50	149	3.115006	102.432	0.011	686	BB	8.1	
51	107+123	0.071140	102.667	0.011	22	BB	11.3	
52	118	1.281861	103.558	0.019	385	BB	7.8	
53	114	0.356901	103.899	-0.008	24	BB	8.1	
54	134	0.076659	104.496	0.006	28	BB	8.3	
55	131+137	0.035547	105.067	0.012	45	BB	7.7	
56	146	0.403681	105.455	0.019	106	BB	7.9	
57	153	2.840417	106.450	0.015	895	BB	8.3	
58	132	0.684852	108.216	0.016	555	BB	8.3	
59	141+176+105	2.702293	109.348	-0.009	515	BB	14.4	
60	129	0.014328	110.015	0.013	16	BB	7.1	
61	130	0.081114	111.250	0.007	20	BB	6.9	
62	163+138+158+	4.417425	112.199	0.010	757	BB	10.6	
63	182	0.697081	112.930	0.018	48	BB	8.5	
64	187	3.900236	113.722	0.023	1328	BV	9.6	
65	166SIS	4.921273	113.888	-0.006	2041	VV	8.8	
66	183	1.816817	114.360	0.019	569	VB	8.3	
67	185	0.465152	116.771	0.018	302	BB	8.2	
68	167	0.037056	117.391	-0.003	9	BB	6.7	
69	202+167+128	0.311932	117.624	-0.006	191	BB	8.0	
70	174+200+204I	11.663553	118.659	0.045	3932	BB	9.5	R
71	177	1.840270	119.537	0.014	492	BB	8.3	
72	171+197	0.363120	120.146	0.008	214	BB	8.2	
73	173	0.037543	121.310	0.023	19	BB	8.2	
74	156	0.070713	121.833	0.019	54	BB	7.5	
75	172	0.576366	122.556	0.028	204	BB	7.6	
76	157+180+199	7.206979	123.651	0.021	2487	BB	8.1	
77	193	0.435179	124.422	0.021	159	BB	8.2	
78	191	0.124112	124.824	0.021	41	BB	7.6	
79	198	0.068043	128.187	0.003	109	BB	0.0	
80	170+190+201	0.939771	128.836	0.007	209	BB	6.4	
81	196+203	4.480081	129.174	-0.008	1660	BB	6.6	
82	208	0.101339	130.523	-0.013	206	BB	4.3	
83	207	0.095886	131.078	-0.015	148	BB	4.7	
84	189	0.036086	131.360	-0.016	47	BB	0.0	
85	195	0.703326	131.705	-0.016	1035	BB	3.5	
86	194	1.901737	133.084	-0.020	2564	BB	3.2	
87	205	0.093067	133.394	-0.020	146	BB	0.0	
88	206	0.724105	134.676	-0.020	995	BB	3.6	
89	209	0.010731	135.533	-0.019	55	BB	3.3	
	Totals:	187.695437		0.651	42619			

Status Codes:
R - Reference peak

Total Unidentified Counts : 6147 counts

Detected Peaks: 293 Rejected Peaks: 6 Identified Peaks: 89

Attachment 2: Mixed Congener Standrd on DB-1701
(Page 5 of 5)

```
Amount Standard: N/A        Multiplier: 1.000000   Divisor: 1.000000
Baseline Offset: -14 microVolts
Noise (used): 50 microVolts - monitored before this run
Rack: 1      Vial: 12       Injection Number: 1    Injection Volume: 5.0 ul
****************************************************************************
```