Analysis of PCBs and Pesticides

in

Air and Precipitation Samples

IADN Project
Gas Chromatography Procedure

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I. INTRODUCTION

This document describes the Gas Chromatographic operation and analyses of PCBs and pesticides in air and precipitation samples collected from six sites on the Great Lakes. This research is conducted at the School of Public and Environmental Affairs, Indiana University, Bloomington, as a part of the Integrated Atmospheric Deposition Network (IADN). The Great Lakes National Program Office of the U.S Environmental Protection Office supports the research.

There are three Gas Chromatographs used for analysis of PCBs and pesticides. These are:

1. **Hewlett Packard GC 5890**. It is referred as **GC South.** Installed on March 7, 1985 in Geology 541
   GC Serial No: 2443A04156

   6890 Series injector and Ni^{63} electron capture detector
   Tower Model No. G1513A
   Tower Serial No. US72202223
   Tray Model No. 18596C
   Tray Serial No. US74002611

   Electron Capture Detector with Ni^{63} K4479 Date 1/98

   The Integrator Hewlett Packard 3396 controls operations of this GC. The GC and the autosampler are connected with Multichannel Interface Hewlett Packard 35900E.

2. **Hewlett Packard GC 6890** Series with an Electronic Pressure Control and Autosampler. It is referred as **GC 1.** Installed in by HP Engineer Thomas Kruzil in June 10, 1999 in SPEA 471
   GC Model No. G1530A
   GC Serial No. US00028275

   Autosampler 7683 Series Injector
   Tower Model No. G2613A
   Tower Serial No. US91907156
   Tray Model No. G2614 A
   Tray Serial No. US91605038

   Micro ECD with Ni^{63} U1303 Date 04 99

3. **Agilent GC 6890N** with an Electronic Pressure Control and Autosampler. It is referred as **GC 2.** Installed by HP Engineer Mike Hartz on March 14, 2005 in SPEA 471
   GC Model No. G1530N
   GC Serial No. CN10505016

   Autosampler 7683 B Series Injector
   Tower Model No. 2913A
   Tower Serial No. CN50423215
   Tray Model No. G2614 A
   Tray No. CN50331934

   Micro ECD Ni 63, U7874 (12/04)

A 60m, DB-5 column with 0.25mm i.d and 0.1µ film thickness is used for good resolution of PCBs and pesticides in 6890 GC1 and GC2. Data acquisition and quantitation are done in Hewlett Packard 3365 ChemStation Revision A.10.02 (1757). Hydrogen and Nitrogen, ultrapure grade, are used as carrier gas and detector make-up gas. A 60m, DB-1701column with 0.25mm i.d and 0.1µ film thickness is used as a second confirmation column in 5890 or GC South.

Hexane fraction of a sample after silica gel cleanup is used for the analysis of PCBs, HCB, p,p'-DDE, p,p'-DDT, t-Nonachlor, aldrin, o,p'-DDT, and Octachlorostyrene. The 50% dichloromethane fraction in hexane is used for analyses of the other pesticides. After GC work the mass of the analytes are calculated by internal standard (ISTD) quantitaion procedure. The ISTDs for PCB analysis are PCB congeners 30 and 204. The ISTDs for the pesticides are PCB congeners 65 and 155.

For every GC run one hexane blank and a calibration standard are run for checking the instrument background and for calibrating the instrument. A second reference standard is also run to check the performance of the instrument. Another calibration standard is run at the end to check the shift of response factor of the instrument during the run. Another hexane blank is run at the end to check the cleanliness of the instrument after the samples are run.

Relative response factors (RRFs) for each analyte are determined from the calibration standard's peak areas using equation,

$$\mathrm{RRF}_{\mathrm{std}} = \left(\frac{\mathrm{mass}_{\mathrm{a}}}{\mathrm{area}_{\mathrm{a}}}\right)_{\mathrm{std}} \div \left(\frac{\mathrm{mass}_{\mathrm{istd}}}{\mathrm{area}_{\mathrm{istd}}}\right)_{\mathrm{std}}$$

Where $mass_a$ is the analyte's known mass in the injected amount of calibration standard, $area_a$ is the analyte's peak area, $mass_{istd}$ is the known mass of the appropriate internal standard, and $area_{istd}$ is that internal standard's peak area.

An analyte's mass in a sample ($mass_a$) is calculated from the RRF_{std} above and the internal standard response in the sample by the following equation:

$$\left(\mathrm{mass}_{\mathrm{a}}\right)_{\mathrm{sample}} = \left(\mathrm{area}_{\mathrm{a}}\right)_{\mathrm{sample}} \times \mathrm{RRF}_{\mathrm{std}} \times \left(\frac{\mathrm{mass}_{\mathrm{istd}}}{\mathrm{area}_{\mathrm{istd}}}\right)_{\mathrm{sample}}$$

where $area_a$ is the analyte's peak area in the sample, $mass_{istd}$ is the mass of internal standard spiked into the sample, and $area_{istd}$ is the internal standard's peak area in the sample.

The routine GC maintenance, daily operation, instrument calibration, and the quantitation are described in the following sections.

II. ROUTINE GC MAINTENANCE

1. Gas Tanks

Check the gas tanks. Tanks should not go dry. While changing the tank, lower the temperature of the GC oven down to 40^0C. Leave it at 40^0C for about 15 minutes after changing the tank to get rid of air or oxygen that was drawn in.

2. Head Pressure

It is electronically controlled in 6890. It should be at 22-24 psi. In 5890 it is manually kept at 22-24 psi.

3. GC oven baking

Before every GC run bake the oven at 280^0C, the injector at 280^0C, and the detector at 380^0C for 1 hour.

4. Septum

a) After every 50- 60 samples or so change the septum.
b) Cool the oven down to 40□C.
c) Remove autosampler tower.
d) Remove septum nut and take the old septum out. Discard.
e) Using clean Q-tips soaked in hexane, wipe off the septum holder.
f) Put a new clean septum and replace the nut. Nut should be snug but not too tight.

5. Background

Background signals in GC 5890 or South GC should be around 20. For 6890 the output is 170-200 mz. Hexane is analyzed at the start of every GC run to monitor the baseline stability. If the signal goes up or hexane run produces noisy chromatogram GC should be cleaned.

6. Standard

Mullin 94 standard or PCB Common Calibration Standard and a Mixed Pesticide Standard should be monitored to check the peak detection and the peak broadening or tailing. If the peak shapes are not satisfactory, column should be clipped. Altogether 128 peaks (including PCBs, pesticides, surrogate and Internal standards) should be detected in Mullin's PCB standards and congener 17, 18, and 77 should be separated. If not, install a new column. For common calibration Standard 60 peaks should be detected.

7. Checking Leaks and Gas Flow in 5890

Check leaks once in two weeks with a leak detector. Check around the septum, at the injector end, and at the detector end of the column.
Check the gas flow once in two weeks with a flow meter. Approximate gas flows are as follows:

Split vent	120 ml/min.
Purge vent	2 ml/min.
Total flow through detector	22 ml/min.

8. Checking Leaks and Gas Flow in 6890

Check leaks once in two weeks with a leak detector. Check around the septum, at the injector end, and at the detector end of the column.

Approximate gas flows are as follows:

Split vent	61.4 mL/min
Total flow	70 mL/min
Initial column flow	2 mL/min
Detector gas flow	20 mL/min

The gas flows are set electronically. Sometimes it is advisable to monitor the gas flow with a flow meter to check if the electronic set up match with the actual flow.

The detailed GC 6890 conditions and method information for DB-5 and DB-1701 columns are printed out and added in the appendix.

III. GC CLEANING

CLIPPING OLD COLUMN OR INSTALLING A NEW COLUMN

1. Taking Apart

a) Turn oven, injector and detector off.

b) Turn hydrogen and nitrogen off manually or electronically. Wait until everything cools down.

c) Take the autosampler tower off.

d) Undo the small nut covering the septum and the large nut underneath it to expose the injection liner. Take the liner out.

e) Open the oven. Take the column out (by detaching from injector and detector ends).

f) Unscrew the nuts from both injector and detector ends of columns and plug the column ends with a septum. **Open end of the column should not be exposed to air.**

g) Place the column on the workbench.

h) Unscrew the holder nut underneath the injection liner. There is one gold seal and a washer in it. The washer and the gold seal need to be replaced each time they are taken apart. Clean these parts by ultrasonication with dichloromethane and hexane and air dry. **This step is done when there is a problem with signal or base line.**

i) Put a beaker inside the oven underneath the injection port and pour some hexane through the injection port. Clean the injection port with Q-tips and rinse again with hexane.

2. Assembling Injection Port and Liner

a) **If step h is performed**, assemble the holder nut. Place the washer first and then the gold seal. The tapered opening of the seal will face downward (the tapered end will hold the end of the ferrule from the column). Screw the nut in before placing the injection liner.

b) Insert a new liner.

c) Put a viton O-ring on the liner. Put the big nut on and tighten it. Put in a clean septum. Cover the septum with septum nut. Tighten with a wrench.

3. Clipping Column

a) Take the nut off the injector end of the column. Carefully scrape out all the ferrules from the column nuts. Clean all different parts with Q-tips soaked in DCM and ultrasonicate these parts with DCM and Hexane for 10 minutes with each solvent. Onto the column, insert the nut first and then a new ferrule with conical end pointing towards the open end of the column.

b) Clip the column. Make a clean cut with diamond tip score or Ceramic Square. Examine the hole with magnifying glass. It should be a clean hole without any jagged end. **Always clip the column after putting the nut and the ferrule on.**

c) Measure **25mm** from the tip of the column. Mark this point with Liquid Paper.

d) Carefully insert the column with nut and ferrule through the holder nut and screw it in. As soon as it feels tight, pull the column out gently until the white mark is seen. Hand tighten the screw more and make it tight with wrench 1/4 turn after hand tight. **Do not over tighten**.

e) Take the nut off the detector end of the column. Remove old ferrule. Put the nut and the new ferrule on the column in the same way as in the injector end. Clip the column and check for the nice clean cut. Turn hydrogen on and check the flow of gas through the column by inserting the cut end in a beaker of hexane. Turn hydrogen off.

f) Measure 71 mm and put a mark with white out. Insert the column until the white mark is seen. Tighten the screw.

4 Checking Leaks and Gas Flow

a) Turn H_2 and N_2 on. Check leaks with a leak detector. Check around the septum, at the injector and at the detector ends of the column inside the oven. Check that the head pressure is 24 psi.

b) Check the gas flow with a flow meter. Approximate gas flows for 5890 are as follows:

Split vent	120 ml/min
Purge vent	2 ml/min.
Total flow through detector	22 ml/min

c) Gas flow in 6890 should be back to electronic initial set up

Split vent	61.4 mL/min
Total flow	70 mL/min
Initial column flow	2 mL/min
Detector gas flow	20 mL/min

5. Assembling

a) Reinstall the autosampler tower.

b) Turn the heated zones on.

c) Turn oven on and set the temperature to 40^0C for an hour. Change oven temperature to 70^0C and

leave another hour.

d) If it is an old column, bake the column, injector and detector for an hour.

Baking temperature:

Oven:	280^0C
Injector A:	280^0C
Injector B:	280^0C
Detector A:	380^0C
Detector B:	380^0C

e) If it is a new column, bake injector and detector. Column should be conditioned by ramping it 1 or 2 degrees per minute to 280^0C. Hold there for 1 hour.

f) If blank run looks satisfactory, check a standard.

IV. ROUTINE GC OPERATION

1. GC condition and oven temperature program:

PCBs, Hexachlorobenzene, p,p'-DDE, aldrin, o,p'-DDT, octachlorostyrene, about 50% of t-Nonachlor, and p,p'-DDT are eluted in the hexane fraction, whereas the other chlorinated pesticides and PAHs are eluted in the 50% dichloromethane in hexane fraction after the silica gel column chromatography. The procedure for nitrogen blowdown, spiking with internal standard, and making microvials for the autosampler are described in IADN Project Sample Preparation Procedure, Version 1.3, and November 2004.

GC 5890 :

Carrier gas:	Hydrogen
Make up gas	Nitrogen
Split vent:	120 ml/min
Purge vent	2 ml/min
Total flow through the detector:	22 ml/min
Column:	DB-5, 60m, 0.25mm i.d, 0.1μ film thickness

GC 6890

Carrier gas:	Hydrogen
Make up gas	Nitrogen
Split vent	61.4 mL/min
Total flow	70 mL/min
Initial column flow	2 mL/min
Detector gas flow	20 mL/min

The detailed GC conditions for the GCs are attached in appendix.

2. Temperature Program for 6890 and 5890

GC 6890, DB-5

Initial temp.	100^0 C
Initial time	1 min.
Rate	1^0 C/min
Final temp.	240^0 C
Rate A	10^0 C/min
Final temp A	280^0 C
Final time	20 min.
Purge time	0.5 min.
Run time	165 min

GC 5890, DB-1701

Initial temp.	100^0 C
Initial time	1 min.
Rate	10^0 C/min
Final temp.	160^0 C
Rate A	1^0 C/min
Final temp A	240^0 C
Rate B	10^0 C/min
Final temp B	260^0 C
Final time	20 min.
Purge time	0.5 min
Run time	109 min.

Mike Mullin specified the GC condition, column type, and the oven temperature program. The method name is Mullin.m

3. GC Pre-run

a) Check if there is sufficient H_2 for operation. If not, change the tank. If necessary, change the septum.

b) Bake oven at 280^0C, injector and detector at 280^0C and 380^0C respectively for about an hour.

c) Cool oven to 100^0C, injector to 250^0C, and detector to 350^0C.

Make the samples ready in microvials and load the autosampler tray.

4. Logging into the computer

a) User name Hiteslab
b) Password ******
c) Domain STC- PV 471-01

5. Preparing Sequence in ChemStation

Open HPChemStation. Open South GC or GCSPEA and then Instrument 1 or 2 (GC1 or GC2)

Method and Run Control	Sequence	Sequence parameter

a) Type in the operator's name and the subdirectory name (Batch ID). Type in the information about calibration standard, dates, and spikes in the comment section.

b) Set the prefix/counter, signal 1: Type in analysis date as prefix. Example J2704 (data acquired on January 27, 2004). Counter should be 001.

c) Prepare a sample table with hexane blank, calibration standard, performance standard, and actual samples with proper ID's. At the end of each sample ID indicate whether the sample is a hexane fraction or 50% fraction with H or F1. Repeat hexane blank and a fresh standard at the end of the sequence. Once a month run a Calibration Reference Standard.

d) Save the sequence in c:\HPChem\1\Sequence as .S file.

An example of a sequence is given on the next page.

Chart 1

A Typical Pesticide Sequence for a GC run

```
Sequence Parameters:

  Operator:

  Data File Naming:              Prefix/Counter
  Signal 1  Prefix:              m3105
  Counter:                       001
  Signal 2  Prefix:              SIG2
  Counter:                       0001
  Data Directory:                C:\HPCHEM\2\DATA\

  Data Subdirectory:             D204CF1
```

```
  Part of Methods to run:          According to Runtime Checklist

  Barcode Reader:                  not used

  Shutdown Cmd/Macro:              none

  Sequence Comment:
    gc2. db-5 pestcalst b16 (2/08/05) pestperfst (10/13/04).  3/31/05.


Sequence Table (Front Injector):

  Method and Injection Info Part:

  Line Vial SampleName       Method   Inj SampleType InjVolume DataFile
  ==== ==== ================ ======== === ========== ========= ==========

    1  1    hexane blank     MULLIN   1   Sample         2.0
    2  2    pestcalst 050331 MULLIN   1   Sample         2.0
    3  3    pestprfst 050331 MULLIN   1   Sample         2.0
    4  4    lbc 050323,f1    MULLIN   1   Sample         2.0
    5  5    eh 01c 041218,f1 MULLIN   1   Sample         2.0
    6  6    sh 01c 041218,f1 MULLIN   1   Sample         2.0
    7  7    th 02c 041218,f1 MULLIN   1   Sample         2.0
    8  8    ch02c1 041218,f1 MULLIN   1   Sample         2.0
    9  9    ch02c2 041218,f1 MULLIN   1   Sample         2.0
   10  10   ph 01c 050123,f1 MULLIN   1   Sample         2.0
   11  11   ph 02c 050123,f1 MULLIN   1   Sample         2.0
   12  12   lh 01c 041218,f1 MULLIN   1   Sample         2.0
   13  13   pestcalst 050331 MULLIN   1   Sample         2.0
   14  14   hexane blank     MULLIN   1   Sample         2.0


Sequence Table (Back Injector):

  No entries - empty table!
```

6. GC run

a) Programming the integrator (5890 GCs only)

The integrator is already edited for the new method with the proper initial parameters. It does not need to be edited for each run. In case of power failure or method change, the method needs to be edited on the integrator as shown below.

Initial parameters:
# of sample washes 2
# of pumps 3
# of solvent A washes 3
# of solvent B washes 3

Shift+Edit method

A menu with a list of options will be shown. Only the following 3 options need to be edited.

#1. Cht sp [1.0]:	Change the chart speed to 0.1 cm/in	This will save paper
#6. Report Option:	Suppress local report? y/n	Select y
#7. Print and post run options	Large font? y/n	Select n (North GC only)

b) Start a 5890 GC run

After saving the sequence in HPChemStation start the instrument with following steps in the computer

HPChemStation | Method and run control | Run Control | Run Sequence

And in the integrator | Shift+ seq | Start

Once the GC makes the injection the sequence will start in ChemStation.

c) Starting a 6890 GC run

HPChemStation controls this instrument. After saving the sequence start the instrument with the following steps in the computer.

HPChemStation | Method and run control | Run Control | Run Sequence

d) Post GC run

The data files (*.d folders) will be saved on C:\HPCHEM\1 or 2 data\. Copy the data on zip disk and transfer to L:\HitesR\GCData\ GCSouth or \GCSPEA (for the 6890)

V. HP 3365 CHEMSTATION GENERAL INTEGRATION AND REPORTING

1. Put all *.d folders in a batch (e.g. D04CH or D04FF1) in individual computer as C:\HpChem\1 or 2\data

2. Open HPChemstation. Go to data analysis.

3. Load Signal

Load a *.d file. The chromatogram will appear on screen.

4. Integration of a chromatogram

Integrate the chromatogram using the following commands:

a) Starting Parameters in Integration Events

Initial slope sensitivity	10	Initial
Initial Peak Width	0.04	Initial
Initial Area Reject	5	Initial
Initial height reject	5	Initial
Shoulder Detection	OFF	Initial
Negative peak on	0.0	

b) Correct the integration by

Baseline now:	This command will maintain a straight baseline.
Area sum on and off:	This command will split a peak if two peaks are not well resolved.
Split peaks	This command will split a peak if two peaks are not well resolved.

c) Printing Integration Event by | File | | Print | | Integration events |

5. Creating Method file

PCB or Pesticide methods are created with proper calibration tables and integration events after integrating the standard chromatograms. The procedures are described in Chapter VI, and Chapter VII.

6. Preparing the Report Template (FRP)

Report Layout	File	New Template	Edit	New Section	General

Header, footer, and a general section will appear. Separate header and footer section by dragging. Put information like method file, data file, injection date and time, operator's name, analyst's name, sample ID etc. on the top of the general section. To do this, click on "abc" and draw a box on the top of the general section. "Select Text" will appear. Click on the following item

From select text

- Method
- Raw data file name
- Injection date
- Injection time
- Calibration and modification date and time
- Acq. operator
- Sample name
- Data Analyst
- Comments

From constant text

From constant text

Put **Chromatogram** in General section by clicking on Chromatogram and set up all options in Set up Chromatogram.

Create a **Table** underneath the chromatogram. Set up the table for Calibrated Compounds. Put the options like mean retention time, main peak type, main peak area, response factor, amount, ISTD, # ISTD, and compound names for the printed columns.

7. Saving Template

File → Save template as as PCB.FRP or Pesticide.FRP. Add the .FRP to Report Style by

File → Add to report style

8. Printing report

After integrating the chromatogram and loading correct method and correct FRP, print a report through **Specify report.** Save the report as ***.txt file in the data folder (***.d folder) together with the method file in C drive.

9. Data storage

After working on the whole batch and saving data in C drive, copy the complete batch files (*.d, *.txt, *.m) in L:\ IADN\CompletedGCdata folder.

V. PESTICIDE DATA REDUCTION IN 50% FRACTION

1. Creating a Method File

a) Integration and Peak Identification

Inject a Mixed Pesticide Standard and load the standard chromatogram in HPChemStation. Correct baseline, integrate, and identify the pesticide peaks (except HCB, p,p'-DDE, aldrin, o,p'-DDT, and octachlorostyrene) from the following Reference Table. This Reference Table was prepared from individual pesticide injection.

Chart 2

Pesticide Reference Table, DB5 Column

Compounds	GC Retention time Min. (approx.)	concentration ng/ml
α-HCH	36	20
Hexachlorobenzene	37	20
β-HCH	41	20
γ-HCH	42	20
δ-HCH	47	20
Aldrin	60	2.5
Heptachloroepoxide	68	20
Octachlorostyrene	67	10
Oxychlordane	69	20
γ-Chlordane	72	20
Congener 155(ISTD)	73	20
Endosulfan I	74	20
α-Chlordane	75	20
t-Nonachlor	76	20
Dieldrin	78	20
p,p'-DDE	82	20
o,p'-DDE	82.7	20
Endrin	83	20
Endosulfan II	84	20
p,p'-DDD	88	20
o,p'-DDT	89	2.5
Endosulfan sulfate	92	20
p,p'-DDT	93	20
Methoxychlor	100	20
Dibutylchlorendate	112	20

Chart 3

Pesticide Reference Table, 1701 Column

Compound Name	GC Retention Time (min)	Concentration (ng/ml)
Hexachlorobenzene	17.5	20
α-HCH	21.4	20
γ-HCH	25.5	20
Aldrin	30.3	2.5
Congener 65 (ISTD)	31.0	20
β-HCH	35.4	20
Oxychlordane	37.6	20
δ-HCH	38.0	20
Congener 155 (Ref)	38.2	20
Heptachlorepoxide	39.8	20
Endosulfan I	43.1	20
γ-Chlordane	44.4	20
α-Chlordane	45.6	20
T-Nonachlor	46.2	20
p,p'-DDE	47.4	20
Dieldrin	48.7	20
Endrin	51.6	20
o,p'-DDD	52.4	20
o,p'-DDT	54.2	2.5
Endosulfan II	59.7	20
p,p'-DDD	60.0	20
p,p'-DDT	62.4	20
Endosulfan sulfate	72.0	20
Methoxychlor	74.0	20
Dibutylchlorendate	75.9	20

b) Preparation of new Calibration Table

If the peak shapes and the integrations in the standard chromatogram look reasonable, prepare a calibration table.

Calibration → New Table

Enter all compound names, amount, and mark congener 155 as reference standard and ISTD.
Set calibration setting to 0.25% for reference and other peaks.
Remove all peaks with zero amounts. **Save file as Method file (Pest. M)**. The calibration table and the integration events will be saved in the method.
Print the calibration table and integration events.

c) Replacing Previous Calibration

Once the calibration table is saved in the method it can be recalibrated and replaced in subsequent GC runs.

Calibration → Recalibrate → Replace

If the GC column has been clipped or running conditions have been changed the analyte peaks shift so much that they are not found in the internal standard report and then a new calibration table will have to be created.

2. Samples, 50% fraction

a) Load Pest. M
b) Load signal from .d file of a sample and integrate (Section V, p12)
c) Load Pest.FRP for **Report style**
d) Check the report on screen first.
e) Print report and save Text File:

Report → Specify Report — Click on printer, screen, and file in Destination. File type should be .txt.

Report → Print Report

Chromatogram and report will be printed.
f) Save Method file in same data folder. The Text File will be saved in the same data folder.
Such as C:\HPChem\1 or 2\data\batch\m30505.d\m30505.m and M30505.txt
Calibration and the integration events will be saved in the method file.

g) Print Integration events File → Print → Integration Events

NOTE: Sometimes it is necessary to increase the window more than 0.25% to find internal standard. If it goes more than 0.5%, rerun the sample in GC.

3. Saving the Data

Copy entire file from C:\ HPCHEM\2\DATA to L:\IADN\Completed GC Data.
First delete .reg, .log, and .mac in each sample folder

A Pesticide Standard Chromatogram, Pesticide Calibration Table, Pesticide Sample Chromatogram, Pesticide Internal Standard Report, and a Pesticide Event are added in the following pages.

Chromatogram 1

Pesticides Calibration Standard Chromatogram, DB5

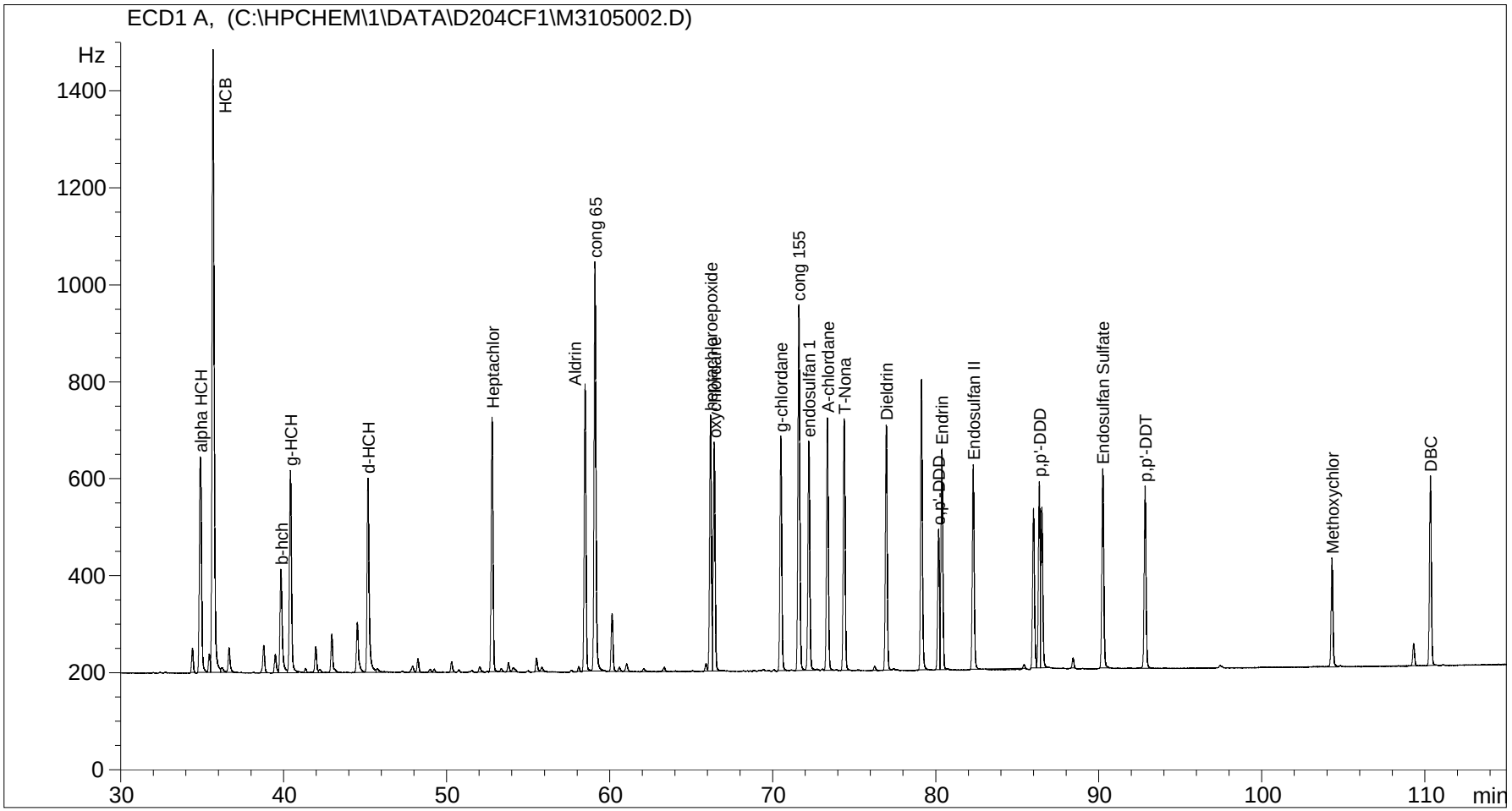


Chart 4

Pesticide Calibration Table, DB5

```
Calib. Data Modified  :      4/5/2005 9:21:12 AM
Calculate             :      Internal Standard
Based on              :      Peak Area
Rel. Reference Window :      0.250 %
Abs. Reference Window :      0.000 min
Rel. Non-ref. Window  :      0.250 %
Abs. Non-ref. Window  :      0.000 min
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      0.00000
Uncalibrated Peaks    :      not reported
Partial Calibration   :      Yes, identified peaks are recalibrated
Correct All Ret. Times:      No, only for identified peaks
Curve Type            :      Linear
Origin                :      Included
Weight                :      Equal
Recalibration Settings:
Average Response      :      Average all calibrations
Average Retention Time:      Floating Average New 75%
Calibration Report Options :
Printout of recalibrations within a sequence:
Calibration Table after Recalibration
Normal Report after Recalibration
If the sequence is done with bracketing:
Results of first cycle (ending previous bracket)
Sample ISTD Information:
ISTD  ISTD Amount   Name
  #      [ng]
----|-------------|------------------------
  1     20.00000   cong 155
Signal 1: ECD1 A,
Signal 1: ADC1 A, ADC1 CHANNEL A
```

RetTime [min]	Sig	Lvl	Amount [ng]	Area	Amt/Area	Ref	Grp	Name
35.836	1	1	20.00000	2.60747e4	7.67028e-4	1		A-HCH
40.943	1	1	20.00000	1.56174e4	1.28063e-3	1		B-HCH
41.435	1	1	20.00000	2.56217e4	7.80589e-4	1		G-HCH
46.305	1	1	20.00000	2.35535e4	8.49131e-4	1		D-HCH
60.263	1	1	20.00000	2.18522e4	9.15239e-4	1		CONG 65
67.361	1	1	20.00000	2.36762e4	8.44732e-4	1		HEPTACHLOR EPOXIDE
67.592	1	1	20.00000	2.33794e4	8.55453e-4	1		OXYCHLORDANE
71.688	1	1	20.00000	2.46206e4	8.12329e-4	1		G-CHLORDANE
72.794	1	1	20.00000	1.74067e4	1.14898e-3	+I1		CONG 155
73.398	1	1	20.00000	2.35293e4	8.50003e-4	1		ENDOSULFAN I
74.539	1	1	20.00000	2.53082e4	7.90258e-4	1		A-CHLORDANE
75.581	1	1	20.00000	2.64377e4	7.56496e-4	1		T-NONA
78.151	1	1	20.00000	2.85323e4	7.00961e-4	1		DIELDRIN
81.366	1	1	20.00000	1.40597e4	1.42251e-3	1		O,P'-DDD
81.563	1	1	20.00000	1.75088e4	1.14228e-3	1		ENDRIN
83.505	1	1	20.00000	2.09667e4	9.53894e-4	1		ENDOSULFAN II
87.551	1	1	20.00000	1.65549e4	1.20810e-3	1		P,P'-DDD
91.454	1	1	20.00000	1.92701e4	1.03788e-3	1		ENDOSULFAN SULFATE
94.045	1	1	20.00000	1.35507e4	1.47593e-3	1		P,P'-DDT
105.501	1	1	20.00000	6402.58740	3.12374e-3	1		METHOXYCHLOR
111.546	1	1	23.15500	1.16684e4	1.98441e-3	1		DBC

Chromatogram 2

Pesticides Calibration Standard Chromatogram, 1701

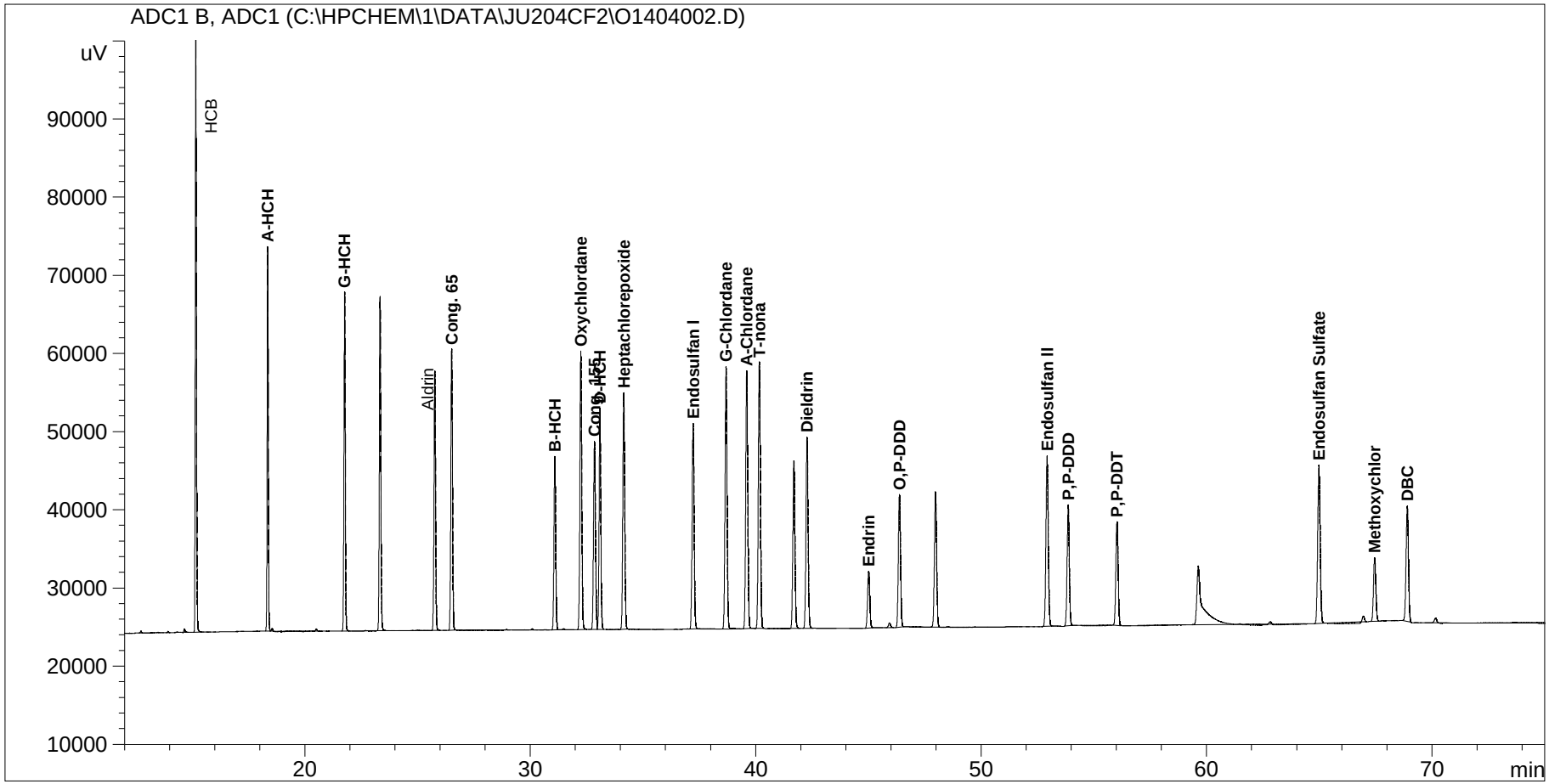


Chart 5

Pesticide Calibration Table, 1701

```
======================================================================
                          Calibration Table
======================================================================
Calib. Data Modified  :      Friday, October 15, 2004 11:05:06 AM
Calculate             :      Internal Standard
Based on              :      Peak Area
Rel. Reference Window :      0.250 %
Abs. Reference Window :      0.000 min
Rel. Non-ref. Window  :      0.250 %
Abs. Non-ref. Window  :      0.000 min
Uncalibrated Peaks    :      not reported
Partial Calibration   :      Yes, identified peaks are recalibrated
Correct All Ret. Times:      No, only for identified peaks
Curve Type            :      Linear
Origin                :      Included
Weight                :      Equal
Recalibration Settings:
Average Response      :      Average all calibrations
Average Retention Time:      Floating Average New 75%
Calibration Report Options :
Printout of recalibrations within a sequence:
Calibration Table after Recalibration
Normal Report after Recalibration
If the sequence is done with bracketing:
Results of first cycle (ending previous bracket)
Default Sample ISTD Information (if not set in sample table):

ISTD  ISTD Amount   Name
  #      [ng]
----|-------------|-------------------------
  1     20.00000   Cong. 65

Signal 1: ADC1 B, ADC1

RetTime   Lvl   Amount      Area     Amt/Area  Ref Grp Name
 [min]    Sig    [ng]
-------|--|--|----------|----------|----------|---|--|--------------
18.353  1  1   20.00000 1.70029e5  1.17627e-4   1    A-HCH
21.764  1  1   20.00000 1.73789e5  1.15082e-4   1    G-HCH
26.511  1  1   20.00000 1.82392e5  1.09654e-4 +I1    Cong. 65
31.090  1  1   20.00000 1.17186e5  1.70669e-4   1    B-HCH
32.241  1  1   20.00000 2.02653e5  9.86907e-5   1    Oxychlordane
32.848  1  1   20.00000 1.43678e5  1.39200e-4   1    Cong. 155
33.091  1  1   20.00000 1.48985e5  1.34241e-4   1    D-HCH
34.147  1  1   20.00000 1.77813e5  1.12478e-4   1    Heptachlorepoxide
37.223  1  1   20.00000 1.61159e5  1.24101e-4   1    Endosulfan l
38.685  1  1   20.00000 2.04081e5  9.80005e-5   1    G-Chlordane
39.603  1  1   20.00000 2.07288e5  9.64840e-5   1    A-Chlordane
40.161  1  1   20.00000 2.15060e5  9.29973e-5   1    T-nona
42.277  1  1   20.00000 1.58651e5  1.26063e-4   1    Dieldrin
45.010  1  1   20.00000 4.95622e4  4.03533e-4   1    Endrin
46.376  1  1   20.00000 1.11490e5  1.79388e-4   1    O,P-DDD
52.927  1  1   20.00000 1.55572e5  1.28558e-4   1    Endosulfan ll
53.863  1  1   20.00000 1.04418e5  1.91538e-4   1    P,P-DDD
56.027  1  1   20.00000 9.27837e4  2.15555e-4   1    P,P-DDT
64.987  1  1   20.00000 1.53966e5  1.29899e-4   1    Endosulfan Sulfate
67.457  1  1   20.00000 5.86038e4  3.41275e-4   1    Methoxychlor
68.907  1  1   23.15500 1.10613e5  2.09334e-4   1    DBC
```

Chromatogram 3

Pesticide Sample Chromatogram
Vapor Phase, DB-5

LH 01C 040820

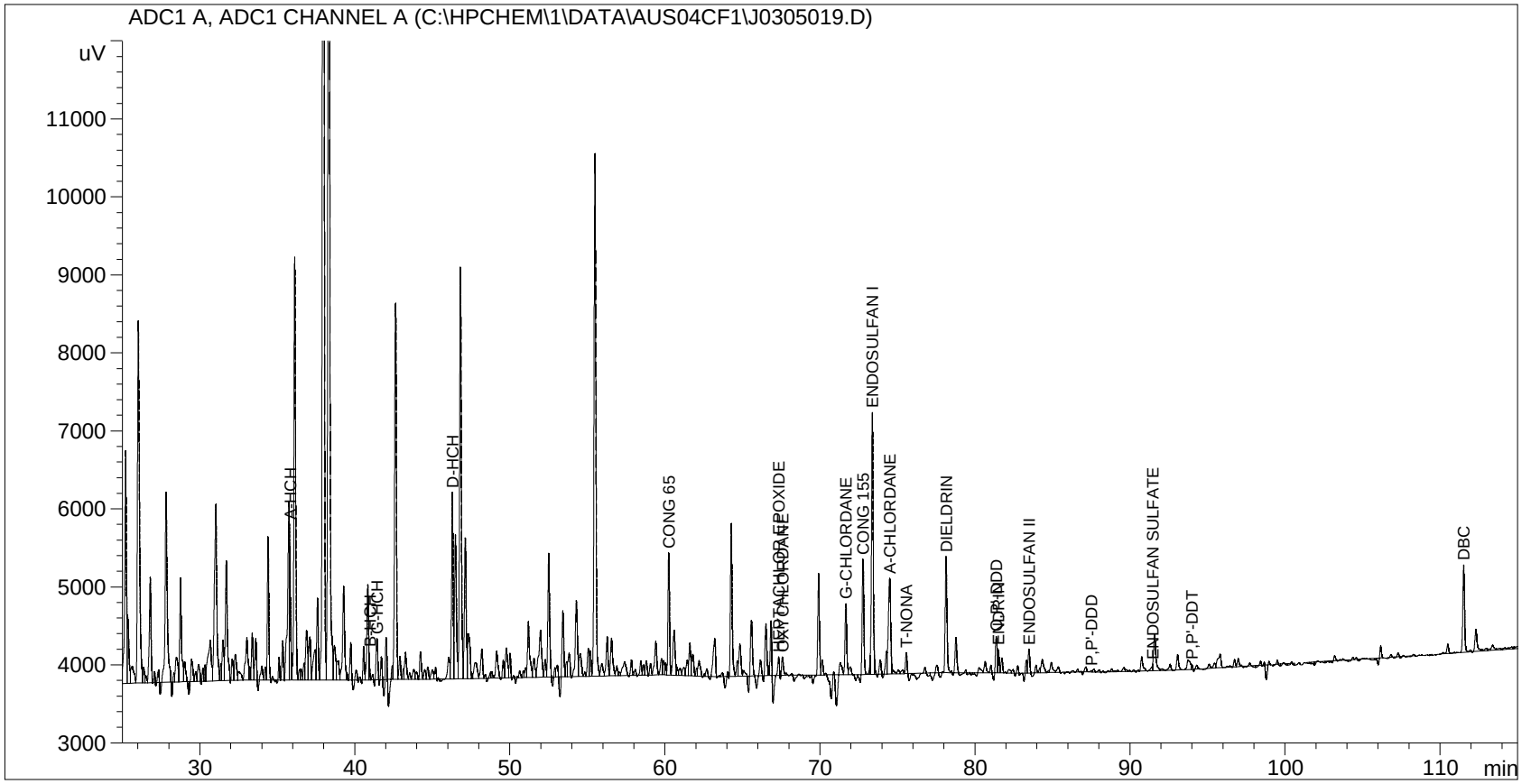


Chart 6

Pesticide Internal Standard Report, DB5

Method File: C:\HPCHEM\1\DATA\AUS04CF1\J0305019.D\J0305019.M
Data File: C:\HPCHEM\1\DATA\AUS04CF1\J0305019.D

Injection Date and Time: 1/5/2005 3:51:49 PM
Calibration Modification Date and Time: Jan 05, 2005 11:59:07 am

GC Operator: Karen Arnold
Data Analyst: J. Rawlinson
Sample: lh 01c 040820,f1
Comments:

Ret. Time (min.)	Peak Type	Peak Area	Rel. Res. Factor	Amount (ng)	ISTD #	Is ISTD	Compound Name
35.842	VBA+	7725	0.668	9.222	1		A-HCH
40.980	VBA+	853	1.115	1.701	1		B-HCH
41.426	PP	3998	0.679	4.858	1		G-HCH
46.290	VV	16628	0.739	21.975	1		D-HCH
60.248	VV	11129	0.797	15.853	1		CONG 65
67.336	PP	1508	0.735	1.982	1		HEPTACHLOR EPOXIDE
67.579	PV	1787	0.745	2.379	1		OXYCHLORDANE
71.674	VV	7166	0.707	9.060	1		G-CHLORDANE
72.777	PBA	11184	1.000	20.000	1	X	CONG 155
73.379	VF	25861	0.740	34.211	1		ENDOSULFAN I
74.499	VF	12856	0.688	15.811	1		A-CHLORDANE
75.568	BP	1851	0.658	2.179	1		T-NONA
78.135	BV	11786	0.610	19.287	1		DIELDRIN
81.368	PV	3688	1.238	8.165	1		O,P'-DDD
81.496	VV	1951	0.994	3.469	1		ENDRIN
83.484	VP	2315	0.830	3.436	1		ENDOSULFAN II
87.500	BV	135	1.051	0.254	1		P,P'-DDD
91.464	BV	489	0.903	0.791	1		ENDOSULFAN SULFATE
93.977	VP	337	1.285	0.775	1		P,P'-DDT
0.000		0	0.000	0.000	1		METHOXYCHLOR
111.522	BV	8836	1.727	27.289	1		DBC

Chart 7
Pesticide Events

```
======================================================================
                        Integration Events
======================================================================

----------------------------------------------------------------------
        Detector Default Integration Event Table "Event_ECD"
----------------------------------------------------------------------
```

Event	Value	Time
Initial Slope Sensitivity	10.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	5.000	Initial
Initial Height Reject	5.000	Initial
Initial Shoulders	OFF	Initial
Negative Peak ON		0.000
Baseline Now		33.679
Area Sum ON		34.668
Area Sum OFF		34.809
Split Peak		35.047
Baseline Now		39.967
Area Sum ON		40.235
Area Sum OFF		40.318
Baseline Now		44.990
Split Peak		45.275
Baseline Now		59.367
Baseline Now		64.245
Baseline Now		66.603
Area Sum ON		70.397
Area Sum OFF		70.550
Split Peak		70.739
Baseline Now		71.315
Baseline Now		72.365
Baseline Now		74.492
Baseline Now		79.675
Area Sum ON		80.115
Area Sum OFF		80.263
Area Sum ON		80.270
Area Sum OFF		80.405
Baseline Now		82.306
Baseline Now		89.858
Split Peak		90.087
Area Sum ON		92.822
Area Sum OFF		93.004
Baseline Now		104.274

```
Apply Manual Integration Events: No
```

Chromatogram 4

Pesticide Sample Chromatogram
Vapor Phase, 1701

CH 02C1 040621

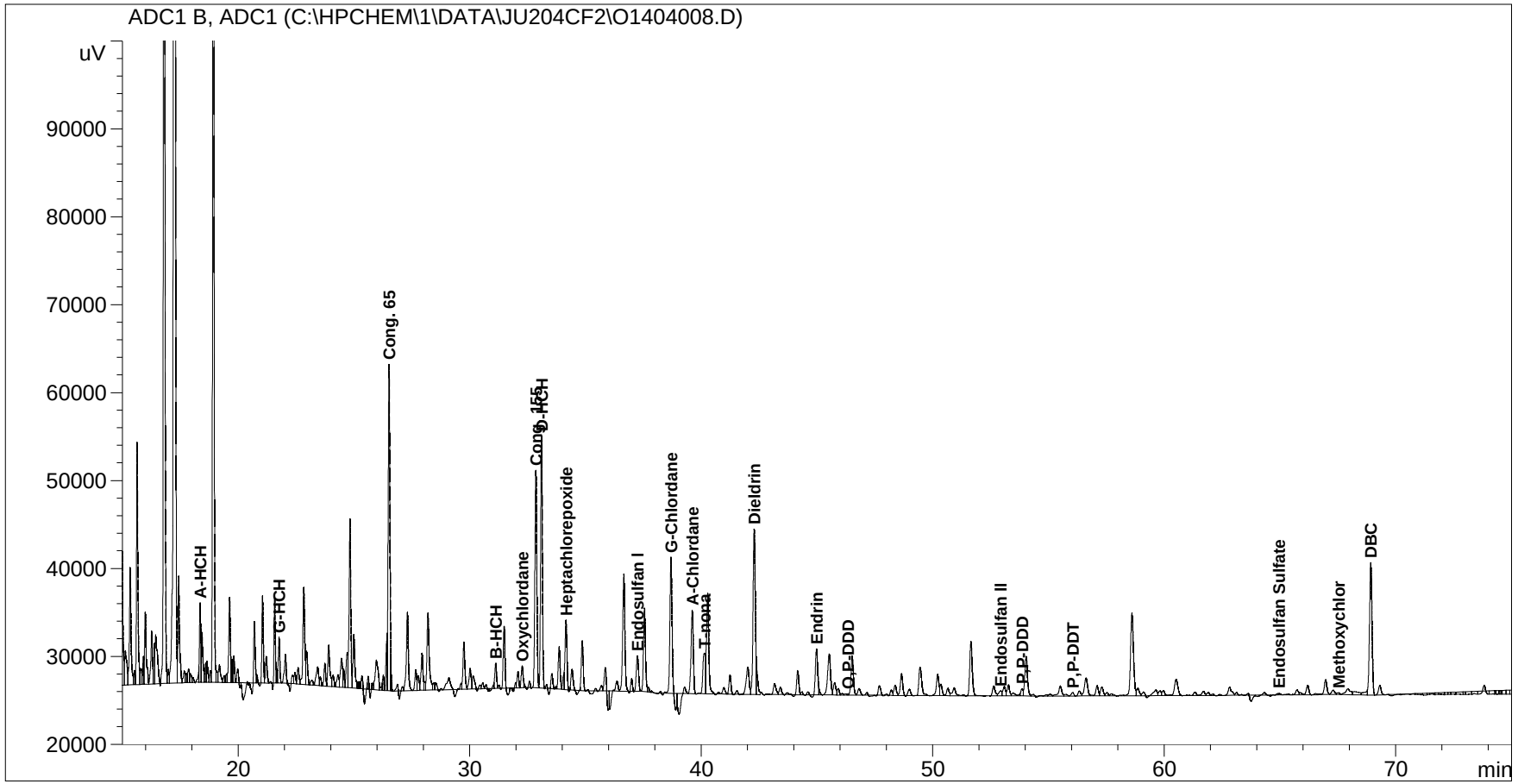


Chart 8

Pesticide Internal Standard Report, 1701

Method File: C:\HPCHEM\1\DATA\JU204CF2\O1404008.D\O1404008.M
Data File: C:\HPCHEM\1\DATA\JU204CF2\O1404008.D

Injection Date and Time: 10/15/2004 2:23:36 AM
Calibration Modification Date and Time: Oct 15, 2004 11:05:06 am

GC Operator: Karen Arnold
Data Analyst: Jenn Rawlinson
Sample: ch 02c1 040621,f1
Comments:

Ret. Time (min.)	Peak Type	Peak Area	Rel. Res. Factor	Amount (ng)	ISTD #	Is ISTD	Compound Name
18.361	VV	33632	1.073	3.795	1		A-HCH
21.77	VV	23600	1.05	2.605	1		G-HCH
26.521	VV	190136	1	20	1	X	Cong. 65
31.129	VV	15472	1.556	2.533	1		B-HCH
32.268	VV	13721	0.9	1.299	1		Oxychlordane
32.862	BP	146052	1.269	19.503	1		Cong. 155
33.106	PP	150419	1.224	19.37	1		D-HCH
34.161	VP	45614	1.026	4.922	1		Heptachlorepoxide
37.249	PP	26872	1.132	3.199	1		Endosulfan l
38.697	VP	98396	0.894	9.25	1		G-Chlordane
39.616	PP	64585	0.88	5.978	1		A-Chlordane
40.145	VV	33702	0.848	3.007	1		T-nona
42.291	VV	126827	1.15	15.337	1		Dieldrin
44.982	PV	36010	3.68	13.94	1		Endrin
46.337	VVA+	476	1.636	0.082	1		O,P-DDD
52.935	VV	5118	1.172	0.631	1		Endosulfan ll
53.859	VV	5191	1.747	0.954	1		P,P-DDD
56.046	VP	3105	1.966	0.642	1		P,P-DDT
64.955	VBA	1138	1.185	0.142	1		Endosulfan Sulfate
67.523	VBA	1576	3.112	0.516	1		Methoxychlor
68.918	VP	113724	1.909	22.837	1		DBC

VII. PCB AND PESTICIDE DATA REDUCTION IN HEXANE FRACTION

1. Creating a Method File

a) Integration and Peak Identification

Inject Mullin 94 Standard which was mixed with (HCB, p,p'-DDE, t-Nona, p,p'- DDT and Aldrin, o,p'-DDT, and Octachlorostyrene).
Load the standard chromatogram and integrate it following the direction in Chapter V.
Identify PCBs from Mullin's 94 chromatogram (Chromatogram 4) and pesticides from individual pesticide standards in Pesticide Reference Table.

b) Preparation of new Calibration Table

If the peak shapes and integration look good prepare a calibration table.

Calibration → New Table

Enter all compound names, amounts supplied by Mike Mullin, and mark congener 30 and 204 as reference ISTDs.

Set calibration setting to 0.25% for reference and other peaks.
Remove all peaks with zero amounts. Save file as **Method File (PCB. M)**. The calibration table and the integration events will be saved in the method.
Print the calibration table and integration events.

c) Replacing Previous Calibration

Once the calibration table is saved in the method it can be recalibrated and replaced in subsequent GC runs.

Calibration → Recalibrate → Replace

If the GC column has been clipped or running conditions have been changed the analyte peaks shift so much that they are not found in the internal standard report and then a new calibration table will have to be created.

2. Samples, Hex fraction

a) Load PCB. M
b) Load signal from .d file of a sample and integrate (Section V, p12)
c) Load PCB.FRP for **Report style**
d) Check the report on screen first.
e) Print report and save Text File:

Report → Specify Report → Click on printer, screen, and file in Destination. File type should be .txt.

Report → Print Report

Chromatogram and report will be printed.
f) Save Method file in same data folder. The Text File will be saved in the same data folder.
Such as C:\HPChem\1 or 2\data\batch\m30505.d\m30505.m and M30505.txt
Calibration and the integration events will be saved in the method file.

g) Print Integration events

File → Print → Integration Events

NOTE: Sometimes it is necessary to increase the window more than 0.25% to find internal standard. If it goes more than 0.5%, rerun the sample in GC.

2. Statistical Calculations

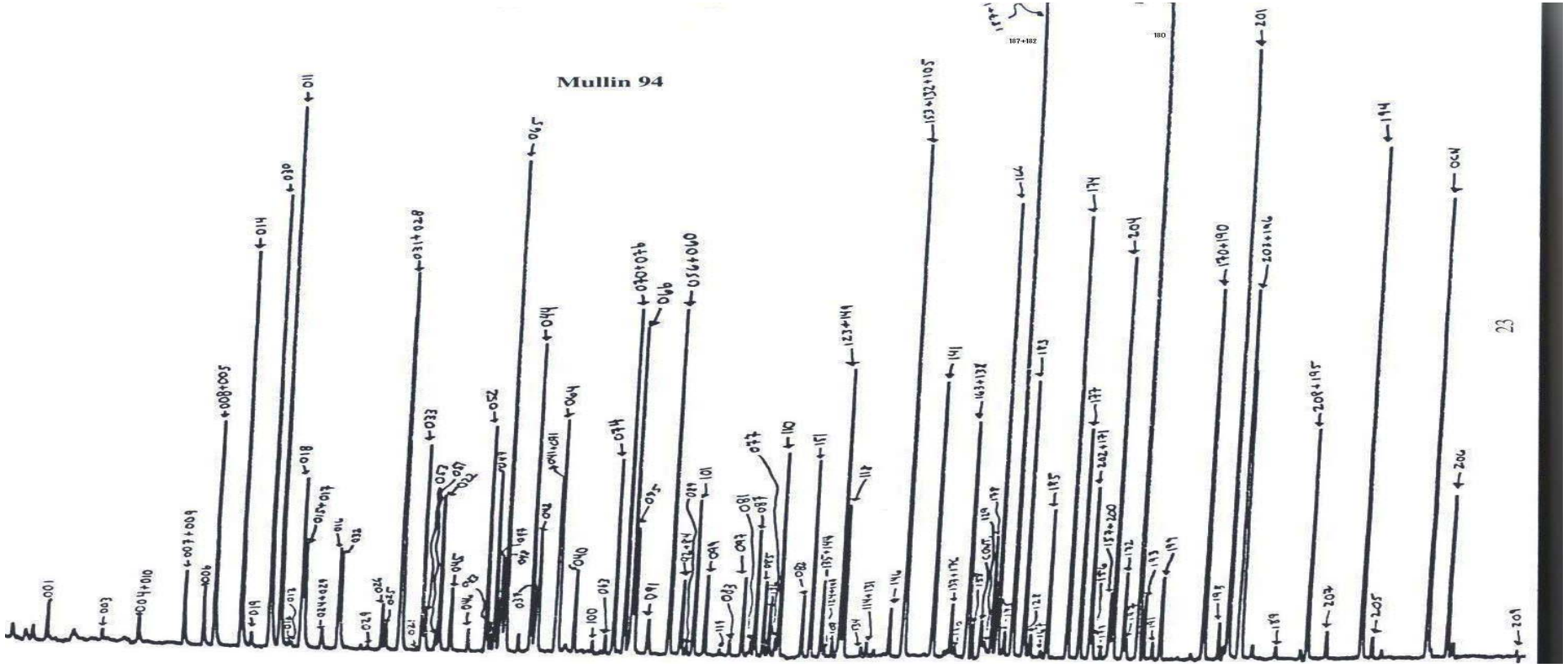
The text files are imported to excel temporarily for statistical calculations. A summary sheet with Total PCBs, percent recoveries of different surrogate standards is generated and printed out.

A Chromatogram from Mike Mullin, PCB Standard Chromatogram, PCB Calibration Table, PCB Sample Chromatogram, PCB Internal Standard Report, and a PCB Integration Events are added in the following pages.

A standard chromatogram of PCB Common Calibration Standard, custom made by AccuStandard, is also added (Chromatogram 7). This standard will replace Mike Mullin's 94 standard. This standard will be used by all IADN participating laboratories.

Chromatogram 5

Mike Mullin's chromatogram



Chromatogram 6

PCB Calibration Standard Chromatogram, Mullin 94

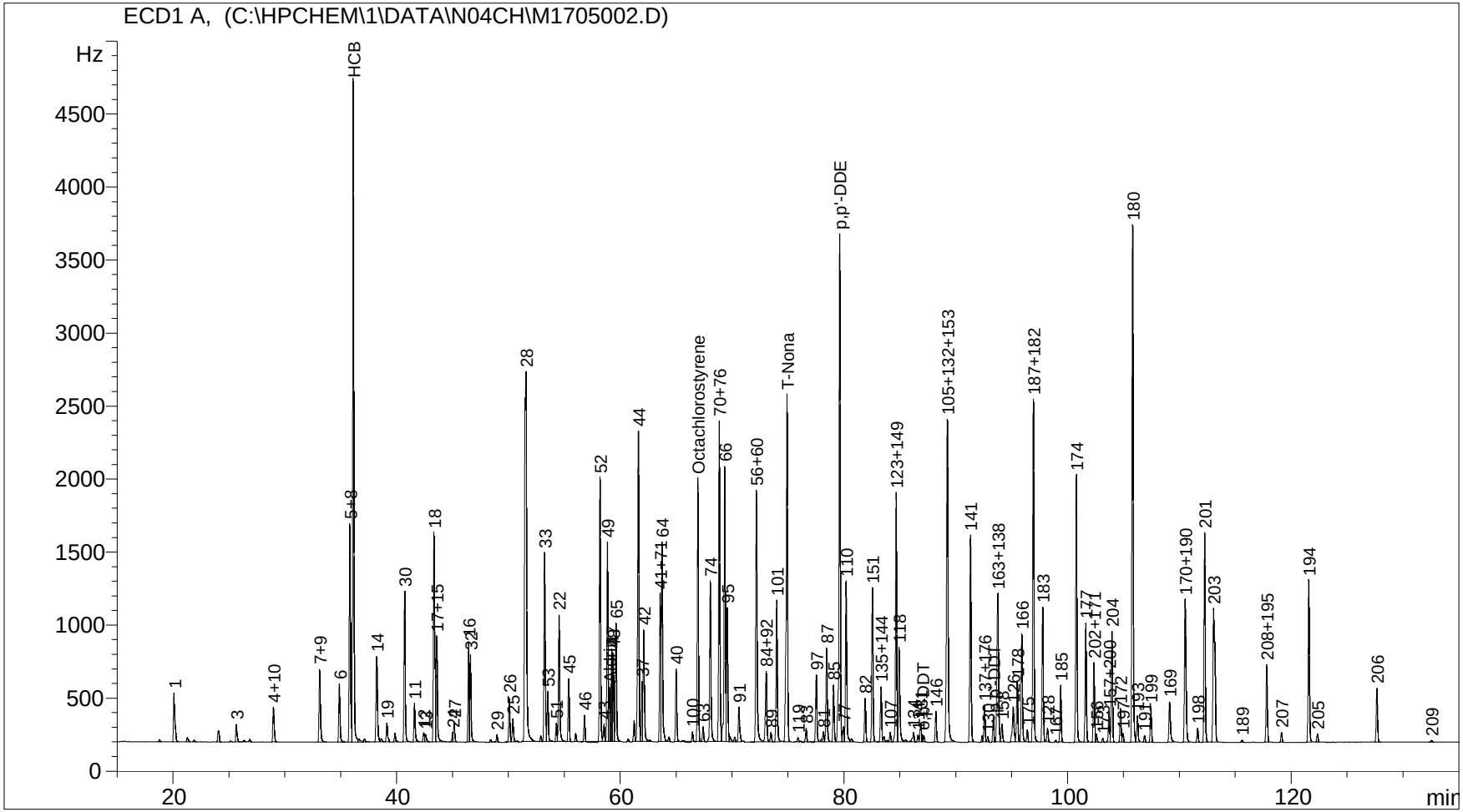


Chart 9
PCB Calibration Table, Mullin 94

```
=====================================================================
                          Calibration Table
=====================================================================

 Calib. Data Modified  :      3/11/2005 10:58:08 AM

Calculate             :      Internal Standard
Based on              :      Peak Area

Rel. Reference Window :      0.250 %
Abs. Reference Window :      0.000 min
Rel. Non-ref. Window  :      0.300 %
Abs. Non-ref. Window  :      0.000 min
Uncalibrated Peaks    :      not reported
Partial Calibration   :      Yes, identified peaks are recalibrated
Correct All Ret. Times:      No, only for identified peaks

Curve Type            :      Linear
Origin                :      Included
Weight                :      Equal

Recalibration Settings:
Average Response      :      Average all calibrations
Average Retention Time:      Floating Average New 75%

Calibration Report Options :
    Printout of recalibrations within a sequence:
        Calibration Table after Recalibration
        Normal Report after Recalibration
    If the sequence is done with bracketing:
        Results of first cycle (ending previous bracket)

Default Sample ISTD Information (if not set in sample table):
ISTD  ISTD Amount   Name
  #    [ng/ml]
----|------------|------------------------
  1      8.00000   30
  2      6.00000   204

Signal 1: ECD1 A,

RetTime   Lvl   Amount      Area     Amt/Area  Ref Grp Name
 [min] Sig     [ng/ml]
-------|--|--|----------|----------|----------|---|--|---------------
 20.090  1  1   48.00000 2404.81958 1.99599e-2   1    1
 25.658  1  1   28.00000  960.37775 2.91552e-2   1    3
 28.985  1  1   13.60000 1907.18665 7.13092e-3   1    4+10
 33.122  1  1    4.80000 4056.95850 1.18315e-3   1    7+9
 34.879  1  1    7.60000 3099.67603 2.45187e-3   1    6
 35.817  1  1   56.00000 1.13778e4  4.92187e-3   1    5+8
 36.122  1  1   20.00000 3.32900e4  6.00781e-4   1    HCB
 38.205  1  1   20.00000 4660.84326 4.29107e-3   1    14
 39.106  1  1    1.12000 1081.20715 1.03588e-3   1    19
 40.694  1  1    8.00000 7570.56201 1.05672e-3 +I1    30
 41.565  1  1   20.00000 2249.76001 8.88984e-3   1    11
 42.386  1  1 6.80000e-1  496.90756 1.36846e-3   1    12
```

RetTime [min]	Lvl Sig		Amount [ng/ml]	Area	Amt/Area	Ref	Grp	Name
42.564	1	1	3.90000e-1	479.86642	8.12726e-4	1		13
43.318	1	1	14.80000	1.27535e4	1.16046e-3	1		18
43.564	1	1	14.80000	5560.30762	2.66172e-3	1		17+15
44.984	1	1	5.20000e-1	344.60672	1.50897e-3	1		24
45.124	1	1	5.20000e-1	998.13409	5.20972e-4	1		27
46.416	1	1	8.00000	4796.22021	1.66798e-3	1		16
46.579	1	1	7.60000	4386.45215	1.73261e-3	1		32
48.942	1	1	2.10000e-1	247.89224	8.47142e-4	1		29
50.050	1	1	2.80000	2306.72510	1.21384e-3	1		26
50.369	1	1	1.30000	1268.92712	1.02449e-3	1		25
51.408	1	1	18.80000	1.42227e4	1.32183e-3	1		31
51.541	1	1	18.80000	1.80453e4	1.04182e-3	1		28
53.208	1	1	13.20000	9966.18359	1.32448e-3	1		33
53.492	1	1	2.60000	2587.53809	1.00482e-3	1		53
54.263	1	1	7.20000e-1	919.74683	7.82824e-4	1		51
54.499	1	1	11.60000	6922.26758	1.67575e-3	1		22
55.367	1	1	3.56000	3199.60254	1.11264e-3	1		45
56.777	1	1	1.60000	1325.54932	1.20705e-3	1		46
58.166	1	1	18.00000	1.33980e4	1.34349e-3	1		52
58.526	1	1	1.10000	927.26312	1.18629e-3	1		43
58.831	1	1	9.20000	1.03974e4	8.84838e-4	1		49
59.002	1	1	2.50000	2352.84131	1.06255e-3	1		Aldrin
59.207	1	1	4.00000	4823.56201	8.29263e-4	1		47
59.336	1	1	4.00000	4248.89063	9.41422e-4	1		48
59.597	1	1	5.00000	6108.24512	8.18566e-4	1		65
61.597	1	1	17.20000	1.76464e4	9.74702e-4	1		44
61.927	1	1	4.80000	3297.83032	1.45550e-3	1		37
62.086	1	1	5.60000	6040.34863	9.27099e-4	1		42
63.551	1	1	9.20000	7409.21533	1.24170e-3	1		41+71
63.708	1	1	7.20000	1.08383e4	6.64309e-4	1		64
64.980	1	1	3.76000	3784.01050	9.93655e-4	1		40
66.421	1	1	4.40000e-1	520.29004	8.45682e-4	1		100
66.924	1	1	10.50000	1.39625e4	7.52015e-4	1		Octachlorostyrene
67.381	1	1	8.40000e-1	811.17682	1.03553e-3	1		63
68.028	1	1	7.60000	9065.38184	8.38354e-4	1		74
68.827	1	1	13.60000	1.75564e4	7.74648e-4	1		70+76
69.319	1	1	20.80000	1.51224e4	1.37544e-3	1		66
69.542	1	1	8.00000	6832.95361	1.17080e-3	1		95
70.588	1	1	2.04000	2025.67114	1.00707e-3	1		91
72.149	1	1	14.00000	1.49770e4	9.34769e-4	1		56+60
73.026	1	1	7.20000	4406.36426	1.63400e-3	1		84+92
73.448	1	1	4.00000e-1	407.81757	9.80831e-4	1		89
73.970	1	1	7.20000	7763.71777	9.27391e-4	1		101
74.717	1	1	2.96000	2538.00513	1.16627e-3	1		99
74.895	1	1	20.00000	1.82026e4	1.09874e-3	1		T-Nona
75.874	1	1	1.10000e-1	161.89046	6.79472e-4	1		119
76.602	1	1	6.00000e-1	662.21210	9.06054e-4	1		83
77.499	1	1	2.24000	3470.75098	6.45393e-4	1		97
78.146	1	1	6.40000e-1	558.53821	1.14585e-3	1		81
78.431	1	1	4.00000	5284.14258	7.56982e-4	1		87
79.048	1	1	2.80000	3097.69482	9.03898e-4	1		85
79.403	1	1	3.00000	1901.59204	1.57763e-3	1		136
79.607	1	1	20.00000	2.63523e4	7.58947e-4	1		p,p'-DDE
79.922	1	1	9.20000e-1	949.79291	9.68632e-4	1		77
80.175	1	1	7.60000	8951.18652	8.49049e-4	1		110
81.881	1	1	1.80000	2490.53027	7.22738e-4	2		82
82.526	1	1	6.80000	8181.35937	8.31158e-4	2		151
83.301	1	1	3.56000	3317.25415	1.07318e-3	2		135+144

RetTime [min]	Lvl Sig	Amount [ng/ml]	Area	Amt/Area	Ref	Grp	Name
84.110	1 1	5.20000e-1	599.26569	8.67729e-4	2		107
84.650	1 1	11.20000	1.35216e4	8.28304e-4	2		123+149
84.919	1 1	4.80000	5905.00244	8.12870e-4	2		118
86.211	1 1	2.90000e-1	582.55560	4.97807e-4	2		134
86.598	1 1	5.20000e-1	443.15234	1.17341e-3	2		114
86.844	1 1	1.20000e-1	1026.03064	1.16956e-4	2		131
87.016	1 1	2.50000	650.06720	3.84576e-3	2		o,p'-DDT
88.198	1 1	1.56000	1701.03906	9.17087e-4	2		146
89.228	1 1	17.20000	2.27447e4	7.56222e-4	2		105+132+153
91.294	1 1	6.80000	1.21274e4	5.60716e-4	2		141
92.552	1 1	1.04000	2000.01440	5.19996e-4	2		137+176
92.839	1 1	3.00000e-1	308.57437	9.72213e-4	2		130
93.343	1 1	20.00000	1800.55750	1.11077e-2	2		p,p'-DDT
93.747	1 1	10.80000	1.13525e4	9.51329e-4	2		163+138
94.113	1 1	1.00000	1077.69922	9.27903e-4	2		158
94.920	1 1	5.20000e-2	215.52225	2.41274e-4	2		129
95.098	1 1	4.00000	2695.12939	1.48416e-3	2		126
95.479	1 1	4.40000	3411.99951	1.28957e-3	2		178
95.888	1 1	5.00000	6398.78516	7.81398e-4	2		166
96.381	1 1	8.00000e-1	718.15088	1.11397e-3	2		175
96.925	1 1	14.40000	1.91051e4	7.53726e-4	2		187+182
97.752	1 1	6.80000	7566.13184	8.98742e-4	2		183
98.189	1 1	4.00000e-1	799.59735	5.00252e-4	2		128
98.905	1 1	1.96000e-1	130.15837	1.50586e-3	2		167
99.357	1 1	1.90000	3153.72974	6.02461e-4	2		185
100.766	1 1	12.80000	1.48712e4	8.60725e-4	2		174
101.607	1 1	6.80000	6752.47559	1.00704e-3	2		177
102.343	1 1	3.16000	4573.58008	6.90925e-4	2		202+171
102.548	1 1	2.60000e-1	480.02850	5.41635e-4	2		156
103.127	1 1	1.50000e-1	201.94193	7.42788e-4	2		173
103.693	1 1	1.56000	1771.54358	8.80588e-4	2		157+200
103.951	1 1	6.00000	6089.20947	9.85350e-4	+I2		204
104.719	1 1	2.24000	1944.76587	1.15181e-3	2		172
104.937	1 1	4.40000e-1	455.02231	9.66986e-4	2		197
105.795	1 1	24.40000	3.02515e4	8.06572e-4	2		180
106.226	1 1	1.68000	1562.09729	1.07548e-3	2		193
106.862	1 1	4.80000e-1	375.00531	1.27998e-3	2		191
107.436	1 1	1.72000	1938.46423	8.87300e-4	2		199
109.091	1 1	4.00000	2926.23218	1.36695e-3	2		169
110.494	1 1	6.80000	9995.81250	6.80285e-4	2		170+190
111.606	1 1	4.80000e-1	775.38434	6.19048e-4	2		198
112.246	1 1	16.80000	1.17468e4	1.43017e-3	2		201
113.042	1 1	8.40000	7997.68408	1.05030e-3	2		203
113.147	1 1	8.00000	4332.80029	1.84638e-3	2		196
115.573	1 1	1.60000e-1	123.46388	1.29593e-3	2		189
117.789	1 1	3.20000	4426.81641	7.22867e-4	2		208+195
119.115	1 1	3.70000e-1	519.23572	7.12586e-4	2		207
121.555	1 1	7.20000	9218.06836	7.81075e-4	2		194
122.330	1 1	4.40000e-1	466.94522	9.42295e-4	2		205
127.652	1 1	2.72000	3095.54565	8.78682e-4	2		206
132.533	1 1	4.80000e-2	93.87072	5.11342e-4	2		209

Chromatogram 7

PCBs in Vapor Sample

CH 02C 041124

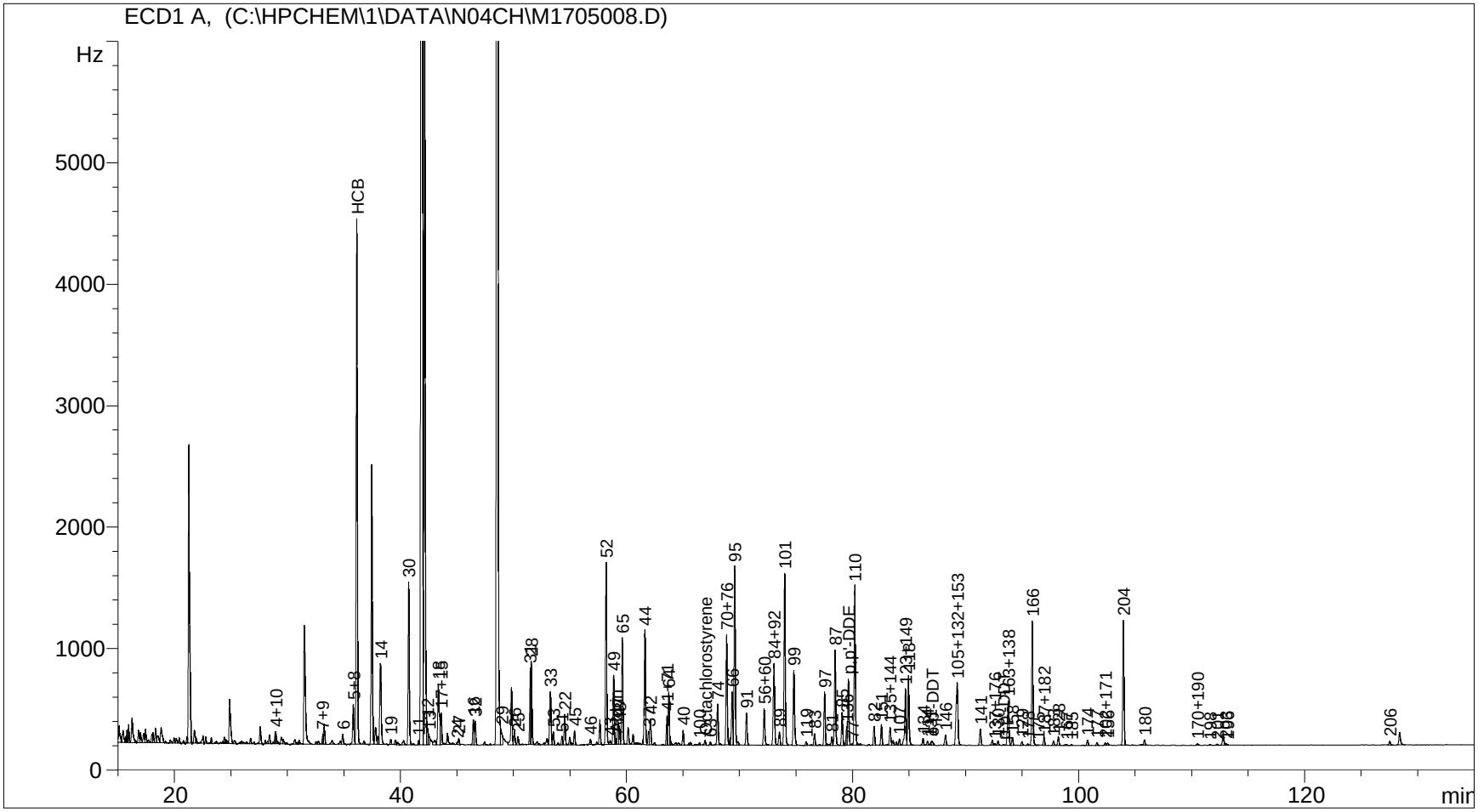


Chart 10
PCB Internal Standard Report

Data File: C:\HPCHEM\2\DATA\N04CH\M1705008.D\M1705008.M
Sample name: ch 02c 041124,h

Injection Date and Time: 3/18/2005 4:2->3/18/2005 4:26:06 PM
Calibration Modification Date and Time: Mar 23, 2005 01:33:57 pm

GC Operator: Karen Arnold
Data Analyst: Karen Arnold
Sample: ch 02c 041124,h
comments: tw= 40.7g, ext wt= 20.8g.

Internal Standard Report

Ret. Time (min.)	Peak Type	Peak Area	Rel. Res. Factor	Amount (ng)	ISTD #	Is ISTD	Compound Name
0.000		0	0.000	0.000	1		1
0.000		0	0.000	0.000	1		3
28.960	VV	558	6.599	3.122	1		4+10
33.096	VVA+	387	1.067	0.350	1		7+9
34.898	VP	601	2.304	1.173	1		6
35.838	PV	2439	4.603	9.514	1		5+8
36.149	VP	31033	0.566	14.877	1		HCB
38.231	VP	5283	4.153	18.595	1		14
39.126	PP	290	1.109	0.273	1		19
40.720	BV	9440	1.000	8.000	1	X	30
41.591	PV	197	8.638	1.445	1		11
42.390	VBA+	1053	1.199	1.070	1		12
42.536	VBA+	587	0.813	0.404	1		13
43.339	VV	5125	1.132	4.917	1		18
43.583	VV	1976	2.313	3.873	1		17+15
45.001	PV	112	1.207	0.115	1		24
45.143	VP	358	0.485	0.147	1		27
46.432	PV	1456	1.562	1.928	1		16
46.600	VP	1368	1.601	1.856	1		32
48.950	VBA+	1106	0.604	0.567	1		29
50.071	VV	828	1.190	0.835	1		26
50.386	VV	502	0.993	0.423	1		25
51.436	VVA+	3824	1.544	5.003	1		31
51.563	VV	4574	0.881	3.415	1		28
53.248	VV	4048	1.253	4.297	1		33
53.513	VP	774	0.904	0.593	1		53
54.277	VV	466	0.777	0.307	1		51
54.520	VV	1793	1.631	2.478	1		22
55.381	VP	802	1.068	0.726	1		45
56.792	PP	303	1.184	0.304	1		46
58.185	PV	11003	1.293	12.059	1		52
58.542	VV	217	1.077	0.198	1		43
58.849	VV	4187	0.857	3.040	1		49
59.040	VVA+	287	0.986	0.240	1		Aldrin
59.228	VV	1438	0.810	0.987	1		47
59.352	VV	1017	0.868	0.748	1		48
59.619	VV	6449	0.774	4.230	1		65

Internal Standard Report

Ret. Time (min.)	Peak Type	Peak Area	Rel. Res. Factor	Amount (ng)	ISTD #	Is ISTD	Compound Name
61.617	VV	6950	0.945	5.567	1		44
61.949	VV	795	1.534	1.034	1		37
62.099	VP	1636	0.847	1.174	1		42
63.567	PV	1721	1.200	1.750	1		41+71
63.724	VV	3318	0.635	1.785	1		64
64.994	VP	881	0.961	0.718	1		40
66.438	PV	120	0.861	0.087	1		100
66.939	VP	281	0.776	0.185	1		Octachlorostyrene
67.395	PP	151	1.063	0.136	1		63
68.045	VV	2528	0.829	1.776	1		74
68.845	PV	6819	0.777	4.488	1		70+76
69.332	VV	3282	1.390	3.866	1		66
69.560	VV	11216	1.066	10.134	1		95
70.601	PP	2045	0.979	1.697	1		91
72.166	PV	2455	0.935	1.946	1		56+60
73.037	PV	6039	1.581	8.092	1		84+92
73.508	VP	948	0.943	0.758	1		89
73.982	PP	11185	0.906	8.585	1		101
74.791	PP	5120	1.346	5.839	1		99
0.000		0	0.000	0.000	1		T-Nona
75.884	BV	241	0.957	0.195	1		119
76.614	VB	737	0.971	0.607	1		83
77.511	PV	3341	0.625	1.771	1		97
78.155	VV	543	1.366	0.628	1		81
78.445	VV	6201	0.754	3.964	1		87
79.058	VV	2074	0.909	1.598	1		85
79.470	VV	958	1.678	1.363	1		136
79.622	VV	4037	0.767	2.622	1		p,p'-DDE
79.945	VV	94	1.009	0.080	1		77
80.189	VV	9839	0.823	6.859	1		110
81.887	PV	1218	0.729	0.675	2		82
82.536	PP	1272	0.820	0.794	2		151
83.307	PV	1212	1.070	0.987	2		135+144
84.127	VV	373	0.994	0.282	2		107
84.663	VV	3866	0.823	2.420	2		123+149
84.930	VB	4582	0.819	2.856	2		118
86.218	PV	434	0.614	0.203	2		134
86.611	VV	251	1.351	0.258	2		114
86.900	VVA+	122	0.104	0.010	2		131
87.016	VV	327	8.616	2.142	2		o,p'-DDT
88.206	PP	691	0.939	0.493	2		146
89.239	VP	6011	0.764	3.492	2		105+132+153
91.289	PP	1102	0.558	0.468	2		141
92.563	VP	88	0.524	0.035	2		137+176
92.844	PP	280	1.113	0.237	2		130
93.345	PP	46	16.265	0.574	2		p,p'-DDT
93.762	PV	3344	0.969	2.464	2		163+138
94.121	VP	503	0.929	0.356	2		158
94.972	PP	226	0.191	0.033	2		129
0.000		0	0.000	0.000	2		126
95.490	PP	88	1.272	0.085	2		178
95.891	PV	8005	0.806	4.906	2		166

Internal Standard Report

Ret. Time (min.)	Peak Type	Peak Area	Rel. Res. Factor	Amount (ng)	ISTD #	Is ISTD	Compound Name
96.383	VP	48	1.178	0.043	2		175
96.930	PP	483	0.759	0.279	2		187+182
97.764	BV	273	0.913	0.190	2		183
98.190	VB	570	0.516	0.224	2		128
98.911	VP	78	2.395	0.142	2		167
99.364	VP	49	0.618	0.023	2		185
100.770	PP	279	0.866	0.184	2		174
101.609	PP	156	1.026	0.122	2		177
102.337	PV	148	0.704	0.079	2		202+171
102.559	VV	150	0.593	0.068	2		156
0.000		0	0.000	0.000	2		173
0.000		0	0.000	0.000	2		157+200
103.952	VB	7888	1.000	6.000	2	X	204
0.000		0	0.000	0.000	2		172
0.000		0	0.000	0.000	2		197
105.805	VB	365	0.833	0.231	2		180
0.000		0	0.000	0.000	2		193
0.000		0	0.000	0.000	2		191
0.000		0	0.000	0.000	2		199
0.000		0	0.000	0.000	2		169
110.502	PP	113	0.705	0.060	2		170+190
111.591	PP	41	0.647	0.020	2		198
112.241	PP	61	1.456	0.068	2		201
113.003	VBA+	84	1.155	0.074	2		203
113.166	VBA+	67	1.671	0.085	2		196
0.000		0	0.000	0.000	2		189
0.000		0	0.000	0.000	2		208+195
0.000		0	0.000	0.000	2		207
0.000		0	0.000	0.000	2		194
0.000		0	0.000	0.000	2		205
127.511	BB	257	0.885	0.173	2		206
0.000		0	0.000	0.000	2		209
				223.247			

Chart 11
PCB Integration Events

C:\Hpchem\1\Data\N04CH\M1705008.d

Signal Specific Integration Event Table "Event_ECD1A"

Event	Value	Time
Initial Slope Sensitivity	10.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	5.000	Initial
Initial Height Reject	5.000	Initial
Initial Shoulders	OFF	Initial
Negative Peak ON		0.000
Baseline Now		14.681
Baseline Now		22.359
Baseline Now		26.597
Area Sum ON		33.020
Area Sum OFF		33.170
Baseline Now		36.623
Baseline Now		40.510
Area Sum ON		42.322
Area Sum OFF		42.453
Area Sum ON		42.463
Area Sum OFF		42.604
Baseline Now		44.803
Area Sum ON		48.849
Area Sum OFF		49.043
Baseline Now		51.172
Area Sum ON		51.346
Area Sum OFF		51.521
Baseline Now		53.790
Area Sum ON		54.090
Area Sum OFF		54.173
Area Sum ON		58.972
Area Sum OFF		59.102
Baseline Now		60.357
Area Sum ON		61.319
Area Sum OFF		61.469
Baseline Now		62.907
Area Sum ON		63.854
Area Sum OFF		64.084
Area Sum ON		77.658
Area Sum OFF		77.790
Area Sum ON		79.230
Area Sum OFF		79.339
Area Sum ON		80.358
Area Sum OFF		80.563
Baseline Now		81.643
Area Sum ON		87.155
Area Sum OFF		87.220
Baseline Now		97.516
Area Sum ON		112.939
Area Sum OFF		113.063
Area Sum ON		113.069
Area Sum OFF		113.263

Apply Manual Integration Events: No

Chromatogram 8

PCB Common Calibration Standard Distributed by Peter Fowlie
(Custom made by AccuStandard, February 2005)
Lot# B5020104, B5020105, B5020115

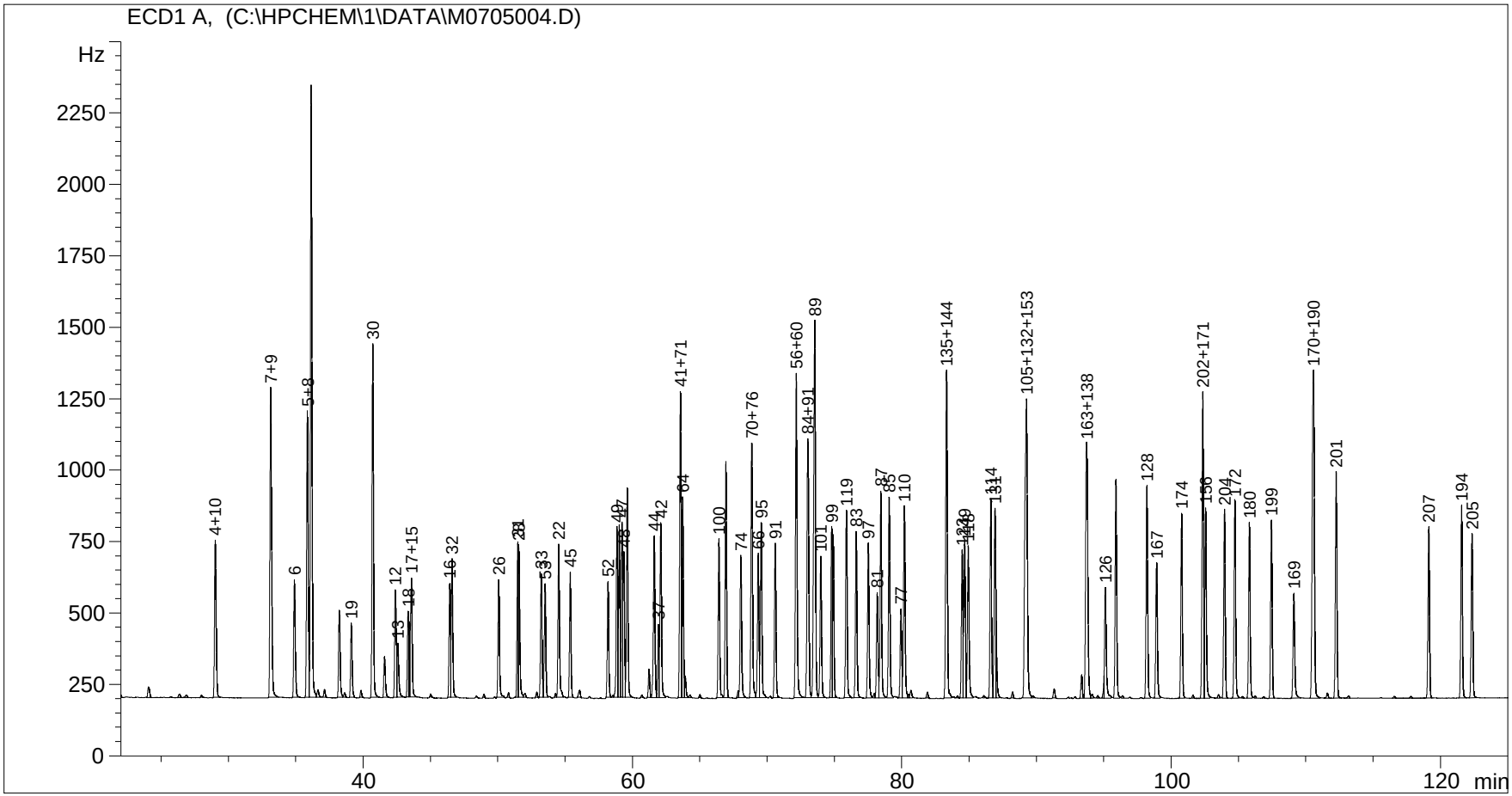


Chart 12

PCB Calibration Standard with Common Calibration Standard

```
================================================================
                        Calibration Table
================================================================

Calib. Data Modified  :      6/14/2005 11:11:09 AM

Calculate             :      Internal Standard
Based on              :      Peak Area

Rel. Reference Window :      0.250 %
Abs. Reference Window :      0.000 min
Rel. Non-ref. Window  :      0.300 %
Abs. Non-ref. Window  :      0.000 min
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      0.00000
Uncalibrated Peaks    :      not reported
Partial Calibration   :      Yes, identified peaks are recalibrated
Correct All Ret. Times:      No, only for identified peaks

Curve Type            :      Linear
Origin                :      Included
Weight                :      Equal

Recalibration Settings:
Average Response      :      Average all calibrations
Average Retention Time:      Floating Average New 75%

Calibration Report Options :
    Printout of recalibrations within a sequence:
        Calibration Table after Recalibration
        Normal Report after Recalibration
    If the sequence is done with bracketing:
        Results of first cycle (ending previous bracket)

Sample ISTD Information:
ISTD  ISTD Amount   Name
  #    [ng/ml]
----|-------------|------------------------
  1      10.00000   30
  2      5.00000   204

Signal 1: ECD1 A,

RetTime   Lvl   Amount      Area     Amt/Area  Ref Grp Name
 [min] Sig     [ng/ml]
-------|--|--|----------|----------|----------|---|--|--------------
 28.705  1  1   20.00000 5250.41406 3.80922e-3   1    4+10
 32.812  1  1   20.00000 1.00285e4  1.99431e-3   1    7+9
 34.564  1  1   10.00000 3497.27368 2.85937e-3   1    6
 35.524  1  1   20.00000 9198.44043 2.17428e-3   1    5+8
 37.888  1  1   10.00000 2576.05542 3.88190e-3   1    14
 38.777  1  1    5.00000 2408.97070 2.07558e-3   1    19
 40.362  1  1   10.00000 9666.42578 1.03451e-3 +I1    30
```

RetTime [min]	Sig	Lvl	Amount [ng/ml]	Area	Amt/Area	Ref	Grp	Name
42.034	1	1	10.00000	3372.72900	2.96496e-3	1		12
42.225	1	1	10.00000	1757.66919	5.68935e-3	1		13
42.988	1	1	5.00000	3532.96899	1.41524e-3	1		18
43.224	1	1	15.00000	4065.15649	3.68989e-3	1		17+15
46.072	1	1	5.00000	3680.14941	1.35864e-3	1		16
46.237	1	1	5.00000	4015.27612	1.24524e-3	1		32
49.700	1	1	5.00000	3406.97339	1.46758e-3	1		26
51.118	1	1	5.00000	3979.47583	1.25645e-3	1		31
51.188	1	1	5.00000	3619.84180	1.38128e-3	1		28
52.850	1	1	5.00000	3995.14722	1.25152e-3	1		33
53.136	1	1	5.00000	3296.14185	1.51693e-3	1		53
54.142	1	1	5.00000	4479.15234	1.11628e-3	1		22
55.007	1	1	5.00000	3692.85791	1.35396e-3	1		45
57.804	1	1	5.00000	3247.84399	1.53948e-3	1		52
58.465	1	1	5.00000	4886.14404	1.02330e-3	1		49
58.842	1	1	5.00000	4860.85254	1.02863e-3	1		47
58.973	1	1	5.00000	4180.07666	1.19615e-3	1		48
59.229	1	1	5.00000	6045.16797	8.27107e-4	1		65
61.229	1	1	5.00000	4618.33447	1.08264e-3	1		44
61.554	1	1	5.00000	2023.53784	2.47092e-3	1		37
61.712	1	1	5.00000	5360.27686	9.32788e-4	1		42
63.172	1	1	10.00000	9726.65137	1.02810e-3	1		41+71
63.338	1	1	5.00000	5784.16748	8.64429e-4	1		64
66.028	1	1	5.00000	4515.53857	1.10729e-3	1		100
67.663	1	1	5.00000	4419.67920	1.13130e-3	1		74
68.463	1	1	10.00000	8434.43652	1.18562e-3	1		70+76
68.945	1	1	5.00000	4405.79492	1.13487e-3	1		66
69.166	1	1	5.00000	5209.24512	9.59832e-4	1		95
70.206	1	1	5.00000	4554.76904	1.09775e-3	1		91
71.766	1	1	10.00000	1.06982e4	9.34735e-4	1		56+60
72.637	1	1	10.00000	9394.47168	1.06446e-3	1		84+92
73.142	1	1	16.00000	1.41933e4	1.12730e-3	1		89
73.588	1	1	5.00000	4347.52100	1.15008e-3	1		101
74.414	1	1	5.00000	4511.85547	1.10819e-3	1		99
75.489	1	1	5.00000	5786.40625	8.64094e-4	1		119
76.215	1	1	5.00000	5097.40283	9.80892e-4	1		83
77.116	1	1	5.00000	5012.86572	9.97433e-4	1		97
77.786	1	1	5.00000	3589.55347	1.39293e-3	1		81
78.050	1	1	5.00000	6378.30957	7.83907e-4	1		87
78.667	1	1	5.00000	6263.62402	7.98260e-4	1		85
79.541	1	1	5.00000	3031.44531	1.64938e-3	1		77
79.797	1	1	5.00000	6450.87256	7.75089e-4	2		110
82.926	1	1	10.00000	1.12593e4	8.88155e-4	2		135+144
84.150	1	1	10.00000	9665.20215	1.03464e-3	2		123+149
84.538	1	1	5.00000	5227.66553	9.56450e-4	2		118
86.213	1	1	5.00000	6402.71338	7.80919e-4	2		114
86.520	1	1	5.00000	6363.84326	7.85689e-4	2		131
88.857	1	1	15.00000	1.62616e4	9.22418e-4	2		105+132+153
93.325	1	1	10.00000	1.23839e4	8.07502e-4	2		163+138
94.723	1	1	5.00000	4435.68262	1.12722e-3	2		126
95.494	1	1	5.00000	7680.59375	6.50991e-4	2		166

RetTime [min]	Lvl Sig		Amount [ng/ml]	Area	Amt/Area	Ref	Grp	Name
97.793	1	1	5.00000	7338.30029	6.81357e-4	2		128
98.518	1	1	5.00000	4902.82422	1.01982e-3	2		167
100.377	1	1	5.00000	6336.05664	7.89134e-4	2		174
101.939	1	1	10.00000	1.05859e4	9.44649e-4	2		202+171
102.157	1	1	5.00000	7210.48730	6.93434e-4	2		156
103.556	1	1	5.00000	6412.06348	7.79780e-4	+I2		204
104.331	1	1	5.00000	7008.43652	7.13426e-4	2		172
105.401	1	1	5.00000	6158.72559	8.11856e-4	2		180
107.039	1	1	5.00000	6337.12939	7.89001e-4	2		199
108.715	1	1	5.00000	4411.28467	1.13346e-3	2		169
110.162	1	1	10.00000	1.73238e4	5.77242e-4	2		170+190
111.851	1	1	5.00000	8128.80225	6.15097e-4	2		201
118.720	1	1	5.00000	6349.51270	7.87462e-4	2		207
121.166	1	1	5.00000	7400.83301	6.75600e-4	2		194
121.929	1	1	5.00000	6554.00879	7.62892e-4	2		205
127.247	1	1	5.00000	6944.82129	7.19961e-4	2		206

5 Warnings or Errors :

Warning : Overlapping peak time windows at 51.118 min, signal 1
Warning : Overlapping peak time windows at 58.842 min, signal 1
Warning : Overlapping peak time windows at 61.554 min, signal 1
Warning : Overlapping peak time windows at 63.172 min, signal 1
Warning : Overlapping peak time windows at 101.939 min, signal 1

Peak Sum Table

No Entries in table

VIII. Appendix

```
==========================================================================

                                6890 GC METHOD
==========================================================================


OVEN
   Initial temp:  280 'C (On)              Maximum temp:  350 'C
   Initial time:  1.00 min                 Equilibration time:  1.00 min
   Ramps:
      #  Rate  Final temp  Final time
      1  1.00      240        0.00
      2 10.00      280        20.00
      3 0.0(Off)
   Post temp:  100 'C
   Post time:  0.00 min
   Run time:   65.00 min

FRONT INLET (UNKNOWN)                   BACK INLET ()
   Mode:  Splitless
   Initial temp:  250 'C (On)
   Pressure:      22.00 psi (On)
   Purge flow:    61.4 mL/min
   Purge time:    0.50 min
   Total flow:    69.1 mL/min
   Gas saver:     On
   Saver flow:    20.0 mL/min
   Saver time:    3.00 min
   Gas type:      Hydrogen

COLUMN 1                                COLUMN 2
   Capillary Column                     (not installed)
   Model Number:        J&W
   Max temperature:     350 'C
   Nominal length:      60.0 m
   Nominal diameter:    250.00 um
   Nominal film thickness:  0.10 um
   Mode:  constant pressure
   Pressure:  22.00 psi
   Nominal initial flow:  1.0 mL/min
   Average velocity:      35 cm/sec
   Inlet:  Front Inlet
   Outlet:  Front Detector
   Outlet pressure:  ambient

FRONT DETECTOR (µECD)                   BACK DETECTOR (NO DET)
   Temperature:  350 'C (On)
   Mode:  Constant makeup flow
   Makeup flow:  20.0 mL/min (On)
   Makeup Gas Type: Nitrogen
   Electrometer:  On
```

SIGNAL 1
Data rate: 20 Hz
Type: front detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: front detector
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
Derive from front detector

COLUMN COMP 2
Derive from front detector

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

GC Injector

Front Injector:

Sample Washes	1
Sample Pumps	3
Injection Volume	2.0 microliters
Syringe Size	10.0 microliters
PostInj Solvent A Washes	3
PostInj Solvent B Washes	3
Viscosity Delay	0 seconds
Plunger Speed	Fast
PreInjection Dwell	0.00 minutes
PostInjection Dwell	0.00 minutes

Back Injector:
No parameters specified