

Chemistry Lab Cookbook

GC Notes, v210.0

Instrument:

HP 6890 - GC3, NGA
 ODP #: 05331, 5330
 Model #: HP6890

Website:

<http://www.agilent.com>

Software:

Chemstation v 9.10

Documentation Available:

Document Name/Title/Number	Source	Version	Associated Instrument(s)	Associated Measurement(s)
Down Hole Contaminants	in-house	n/a (Leg 103)	Gas chromatographs	n/a
Electronic Pressure Control in Gas Chromatography	Hewlett-Packard	Third printing, 4/1995	Gas chromatographs	n/a
GC #3 5890/6890 Binder	in-house	n/a	Gas chromatographs	hydrocarbons
GC Calibrations & Std Binder	in-house	n/a	Gas chromatographs	n/a
GC Packed and Capillary Columns	in-house	n/a	Gas chromatographs	hydrocarbons
GC2 Std/Analysis	In-house, Hewlett-Packard	n/a	Gas chromatographs	n/a
HP 35900B Dual Channel Interface Operating Manual	Hewlett-Packard	Sep-88	Gas chromatographs	n/a
HP 5890 Series II Gas Chromatograph Service Manual	Hewlett-Packard	1st edition, 3/1991	Gas chromatographs	n/a
HP 6890 Series Gas Chromatograph Operating Manual (Volume 1., General Information; Volume 2., Inlets; Volume 3., Detectors)	Hewlett-Packard	Volume 1.: 2nd edition, 12/97; Volume 2.: 1st edition,	Gas chromatographs	n/a

10/96;
Volume 3.:
1st edition,
10/96

HP 6890 Series Gas Chromatograph Service Manual	Hewlett-Packard	2nd edition, 5/1997	Gas chromatographs	n/a
HP 6890 Series Gas Chromatograph Site Preparation and Installation Manual	Hewlett-Packard	1st edition, 4/98	Gas chromatographs	n/a
HP 6890 Troubleshooting and Maintenance Student Manual	Hewlett-Packard	Mar-97	Gas chromatographs	n/a
HP ChemStation Misc. Binder	In-house, Hewlett-Packard	n/a	Gas chromatographs	n/a
HP ChemStation Revision Upgrade Box Set: Installing Your Data Analysis ChemStation; Installing Your A/D Chemstation; Installing and Understanding Your HP Chemstation; Understanding Your ChemStation	Hewlett-Packard	Rev. A.06.01; May, 1998	Gas chromatographs	n/a
Hydrocarbon Monitoring & Safety Binder	in-house	n/a	Gas chromatographs	hydrocarbons
Installing Your A/D ChemStation	Hewlett-Packard	2nd edition, 11/1995	Gas chromatographs	n/a
Installing Your GC Chemstation	Hewlett-Packard	May-98	Gas chromatographs	n/a
Installing Your HP Chemstation	Hewlett-Packard	May-98	Gas chromatographs	n/a
Macro Programming Guide	Hewlett-Packard	2nd edition, 11/1995	Gas chromatographs	n/a
Understanding Your ChemStation	Hewlett-Packard	3rd edition, 11/1995	Gas chromatographs	n/a
Using The HP-IB Interface and Command Library with DOS	Hewlett-Packard	2nd edition, 12/1991	Gas chromatographs	n/a
Valco Valves Binder	in-house, Valco	n/a	Gas chromatographs	n/a
HP Automatic Liquid Sampler Operating Manual	Hewlett-Packard	Oct-95	Gas chromatographs, GC/MSD	n/a

Notes from HP G1200A Chemstation operation class

September, 1994

ANALYTICAL INSTRUMENT CONFIGURATION

must identify HP-IB address (HPIB board/HP35900C)

must name the instrument

Path

creating new subdirectory in path before creating the same subdirectory in File Manager

if deleting a subdirectory or method, make sure it was not the active file in the program before closing the instrument session

INSTRUMENT

Acquire Data - Execute a pre-run program

Analyze Data - Archive files

Report Result - Execute a post-run program

METHOD

Current Method

method which is currently running in memory

modified method is different from the method which is under the same name in the memory

unless "SAVE" is executed for a modified method, the modification will be lost when loading another method

when start a run, all aspects of the analysis are controlled by the current method

Default Method

read-only file cannot be altered and saved

when load default method, instrument parameters are not downloaded to the devices connected to the Chemstation

Stop - stop data acquisition, but run still continues

Abort - stop data acquisition, abort the entire run

DATA ANALYSIS

Specify Report

In version 3.34, one has options to save an integrated chromatogram as an ASCII file with the same name as a text file. It is saved with .WMF extension, and it can be exported to other graphic programs

assign export destination

List File Info

when enter comment under Sample/Info, it is printed out on the first generated report, but not saved with all other information. When export the result file as an ASCII file in other word process program, comment can be copied and pasted through clipboard to other word process program

List Data

collect every single data point generated by the analysis, all points were used by the program for calculation. It is very useful for troubleshooting.

Windows

The display of the chromatogram

default assignment is

#1 lower half of the screen

#2 upper half of the screen

#3 full screen

#4 upper quarter of the screen

use Redefine Window to reassign window position, but this can not be saved. Once leave the Main Screen, program automatically reset all four windows to default.

Register

stack the four most recent files, W, X, Y, Z

one register can contain more than one objects (use MERGE command)

Annotate

after type in the text, click ADD and click at the desire position on the chromatogram

to move it, go back in annotate, click EDIT, notice the text is now highlighted, select the new position

annotate will not be saved with the chromatogram under .WMF file.

Integration

determine the difference between real signal and noise

Qualitative ratio 3 x (S/N)

Quantitative ratio 10 x (S/N)

(S - signal and N - random noise)

this is comparison between max and min signal in a specific period of time, and it is under the condition of ideal (no other interference)

Three types of baseline:

chromatographic signal

integration signal

electronic or absolute (from GC)

only the integration baseline can we manipulate and edit

Solvent ON/OFF (tangent ON/OFF) is mainly for over riding the default parameter for small peaks coming out on the tailing of a large peak. It has to be set before the beginning of the large peak.

Shoulder ON/OFF is for small peaks coming out in the front of a large peak. It has to be assigned before the start of the large peak.

Baseline All Valley sets all baseline in valley, useful for baseline drift from oven program

Baseline Back is to call baseline back to it initial parameter

Peak Width, although it is a time event, it changes gradually instead of efficiently, example of setting pw of 0.4 at 30 minute

minute 1	2	5	10	20	30	
pw	0.04	0.06	0.08	0.1	0.2	0.4

If more than 5 timed integration events (excluding the 4 initial settings). It usually suggest the chromatogram is not optimized, unless it is specified necessary.

SEQUENCE

updating the Sequence table and/or Sample table, it affects the Sample Log Table directly

autonaming	<u>001</u>	<u>F</u>	<u>01</u>	<u>01</u>	
	vial position	signal	sequence line	Inj/vial (repeats)	
	(individual vial)	(can be R)	(injection #)		

sequence line acts like a subsequence. It allows one to use the same method and run as many vials (and as many times of each vial) as one wants.

when using explicit re-calibration, the later run STD will replace the previous same STD run

Seq.	vial	sample	inj
1	1	STD A	1
2	2	unk 1	1
2	3	unk 2	1
2	4	unk 3	1
1	1	STD A	1

when run a single sample manually, the Chemstation uses the "current method" whichever is running currently. But when run sequence, when "Run Sequence" is selected, the Chemstation will (1) erase the current method, and (2) load the method from its memory according to the assigned method in the sequence table.

FILE

.SMP - sample information
 .SEQ - sequence table
 .CAL - method, calibration
 .CHR - method, instrument parameters
 .DRN - method, data analysis parameters
 .EVT - method, integration setpoints
 .MTH - method, fundamental run information
 .RCL - method, recalibration information
 .RPT - method, chromatogram and report output definition information
 InstConf.INI - instrument, internal configuration and connected device

LAB EXERCISE

- (1) If make changes in method in OffLine Copy on integration parameters and save, it will update the method. When upload the method or run a sequence into ONLine , the changes made will be active
- (2) Oven equilibrating time, 3 minutes default for packed column and 1-1.5 minutes default for capillary column.
- (3) Procedure to follow when optimizing integration: initial threshold-initial peakwidth - initial area rejection - timed program - manual
- (4) when using manual integration, "MM" will listed as TYPE in the result report
- (5) Multilevel calibration curve, when linear combine with force origin, R2 is always =1. Ideally, don't force nor include origin but use it as interpretation of blank difference.
- (6) when run sequence recalibration, In the sequence table, the number entered under Recalib interval tells the system to recalibrate each time the number of lines is run, the line listed in the table regardless how many time of injections is entered in each line.
- (7) Sequence: When reprocess a sequence, the reprocessed files will be called out from the subdirectory assigned in the sequence table and the new reprocessed files will over-write the original files for the same autonaming system. To avoid this, copy the original files to another subdirectory before reprocess.
- (8) "Explicit recalibration" means irregular re-calibration, specific placing STD in between the sequence, cal line#. Method has to exist for this to be processed.

Reminder on EPC system for Gcs

Leg163, Oct 1995

1. **EPP C:** control the total He (carrier) flow goes into the GC
EPP B: function as a back pressure control at the split vent
EPP D: control carrier gas flow into valve#3, column head
Total control knob: control the flow goes into the column
Septum purge: should be constant, difference can only be noticed when purge is turn on/off.
split ratio: (column flow)/(column flow+split vent flow)
2. On GC#3, one EPP is installed at Channel A (same model as EPP C on GC#2 and NGA). The flow can be adjusted either by this EPC or by changing the column head pressure. We are using **EPP A** to control and program the flow during a run.
3. On both GC#2 and NGA, changing EPP B will change the split vent flow significantly, but very little for the split ratio. However, changing total control changes the split ratio dramatically.
4. Split ratio only matters when the purge is turn on from Chemstation. When the purge is OFF, it is splitless. It is a good idea to turn the purge on immediately after sample injection to clean the inlet, even running on splitless mode.
5. To ZERO EPC. First make sure there is absolutely no flow going thru the system. The detail please see HP5890 Series II and HP5890 Series II plus reference manual (Site Prep/Installation manual, electronic flow sensing 4-4)
6. To CALIBRATE EPC on GC#2 and NGA, have EPP C wide open (high setting, ie. 40-80psi), adjust "total control knob" and EPP B to obtain the split ratio desired. Please refer to the scatch notes from Leg158 in blue books for each instrument.
7. Remeber that EPP C should always be 5 psi HIGHER than EPP B to avoid systematic error (chirping).

Procedure for entering gas data into JANUS (both GC3 and NGA)

1. In HP Chemstation, enter sample ID in “Sample Info” under “Run Control”. In the Comment Window, enter the sample ID (the format is very important, as this is parsed directly in JANUS). The fixed digit used for each infor is the number in the bracket
LEG(3)SITE(4)HOLE(1)CORE(3)TYPE(1)SEC(2)WR(as whole round)TOP-BOT(no limit)HS.
For example 1801108B010R01WR126-127HS

2. In HP Chemstation method “Runtime check list”, make sure both “Save GLP data” and “ Post run command/Macro [GC3_CSV]” are checked.

3. To ensure the macro is loaded (or to activate the macro), in command line type “MACRO GC3_CSV.MAC, GO” and press enter.

4. Both macros are in C:\Hpchem\Core folder.

5. The macro will generate a CSV file at the end of each GC run, and it looks like this:

1801108B010R01WR126-127HS

C:\HPCHEM\GC3\DATA\LEG180\1108\10R1.D

18-Jun-98, 09:53:34

GC3 FID1 B

901.6	,	C1
0.0	,	C2=
0.0	,	C2
0.0	,	C3=
0.0	,	C3

6. The CSV file is automatically generated under the path

C:\HPCHEM\GC3\DATA\JANUS\gc300#.csv. The # is a counter. It can be set at any given number. To do this, open C:\HPCHEM\Core\Csv_gs3.dat in Notepad. Set the number to desired number (we normally reset it to zero in the beginning of the cruise or each site) and save the file. Repeated file number will create an error.

7. When finish a GC run, go to JANUS-Chemistry-Gas. Select “File Input” under Mode. Query the desire CSV file under “Enter Input File”. Press “Read File”. The sample ID and data will be loaded, and a Status window will appear. If there is a verification problem, the error will appear in red instead of black. If everything is loaded properly, press “Save Input” to load the data into the database. Again, message will appear in the Status Window.

8. And you are done.....

Leg 185 GC2/ECD Set Up Summary

The HP 5890 Series II GC2 was brought from the Chemistry Lab to the Microbiology Lab to analyze perfluorocarbons from contamination tests. It is now named GC2/ECD.

In the HP Configuration, GC2/ECD is configured as Instrument 1 with an HPIB address of 14. A new ECD directory was set up with Methods, Data, and Sequence subdirectories while the old GC2 directory was renamed GC2_OLD and archived both on the C:\ drive of PC124 and in the Chem Lab folder on the TECH Volume.

GC2/ECD was plumbed directly from the back of the instrument to a Nitrogen bottle with Alltech Oxy-trap and a molecular sieve S-trap in line.

During Leg 184, GC2 was fitted with an Electron Capture Detector (ECD), a flow manifold block assembly and an ECD chemical filter, but it was never tested. Proper ratio of make up/anode purge gas for the ECD took time to establish but the problem was solved once a leak was fixed at the o-ring connecting the N2 carrier tubing to the ECD chemical trap.

At the beginning of this Leg, the GC was configured for alkenone separation with a 50m x 0.2mm x 0.11mm film Ultra 1 cross-linked methyl silicone gum column. The Autosampler was connected to the inlet. It was decided quickly by scientists to do manual injections so the autosampler was removed. It is now stored above the GC/MSD.

The HP Ultra 1 column was replaced by the Al₂O₃ HP PLOT column (used to be in NGA before Leg 170) at the request of the scientists. The column dimensions are: 15m x 0.53mm (ID) x 15mm film. Nitrogen was chosen by the scientists as the carrier gas.

With the new column in place, the EPC which regulates the capillary inlet flow, could not keep up pressure. A leak was suspected at the injector. The injector was cleaned, a new liner and gold seal were installed, but the EPC still could not keep up pressure. It was then noticed that the total flow knob had been turned off completely (thank guys!). Opening the total flow and adjusting the EPPC and EPPB to lower settings, than those used with the Ultra 1 column, did the trick. The column was baked out several times using PLOTBAKE.m. See GC2/ECD Book #1 for details.

Method development was long and tedious. As we had no standard procedures for PFTs separation on PLOT column, the approach was basically trial and error. Instrument parameters were mostly derived from Colwell *et al.* (1992). Most of the testing was done by the two scientists.

The GC2/ECD method in use is called ECD_185.m. The run time is 4.5 min.

Operating parameters are as follows:

- Nitrogen supply at bottle: 50 psi;
- EPPC: 10 psi;
- EPPB: 3psi.;
- Column flow : 6.7 ml/min
- Septum purge flow : 3 ml/min
- ECD make-up flow: 69.9 ml/min
- Anode purge flow: 6.9 ml/mn (anode flow automatically sets itself to 1/10 of the make up flow value)
- Injector temperature:180°C;
- Initial Oven Temperature: 120°C, no hold;
- Oven Temperature Ramping: 20°C/min to150°C, hold time of 3 min;
- Detector temperature: 250°C.

The samples/standards were manually injected using either 500 μ l or 5 ml gas-tight syringes (Hamilton). The injection was splitless.

Quantification of the perfluorocarbon was done based on a set of standards prepared as indicated below.

Perfluoro(cyclomethyhexane) standards were prepared by diluting 100 μ L of the PFT with 9.9 mL of methanol in a headspace vial (=10⁻² vol:vol). The vial was mixed on a vortex mixer for 1 minute. Serial dilutions using 100 μ L of the previous solution diluted with 9.9 mL of methanol resulted in a series of PFT solutions (10⁻⁴, 10⁻⁶, 10⁻⁸, 10⁻¹⁰, 10⁻¹² vol:vol). Each headspace vial was thoroughly mixed prior to transferring the 100 μ L to the next vial.

From these standards, 15 μ L were added to 15 mL of distilled water in headspace vials and immediately sealed. The vials were heated at 70°C in an oven and aliquots (50, 500 or 5,000 μ L) of the headspace were injected into the GC using gas-tight syringes that were also heated in the oven. The total amount of PFT injected into the GC was calculated based on the PFT dilution in the vial and the fraction of the headspace that was injected.

The perfluorocarbon retention time on the column is around 2.7 min. Measured peak area is linear with PFT headspace abundance over four orders of magnitude. Based on duplicate analysis of standards, the relative measurement error is 20% and the detection limit approximately 10⁻¹² g PFT.

Sample Analysis was done on hard rock and sediment samples.

Whole rock samples and the crushed interior sections of the rocks were heated at 70°C and 5mL of the headspace gas was removed and injected into the GC. After injecting, the vials were weighed to determine the total amount of rock in each vial.

Sediment samples were collected with a toothpick from a whole round at the bottom of a core section on the catwalk. From each whole round, a sample was taken between the core liner and the core, from the center of the core and/or midway between the interior and the exterior of the core. These samples were immediately placed into headspace vials and sealed. Both the headspace vials containing the sample and the gas tight syringes used to inject them were heated to 70°C in an oven. Five ml of headspace gas was drawn and injected into the GC. After the analysis, the vials were weighed to determine the amount of sediment in each vial. The amount of PFT in each vial was normalized to the weight of the sample. The headspace volume was calculated by subtracting the volume of sediment from the total volume of the vial. The total PFT in each vial was calculated by dividing by the fraction of the total headspace that was injected.

For more details, refer to the GC2/ECD PFT Analyses binder, GC2/ECD blue book, Leg 185 Microbiology Lab Tech Report and Leg 185 Microbiology Contamination Report

Leg 185 GC3 Set Up Summary

GC3, a 5890 Series II Plus GC, was replaced this Leg by an new HP 6890 Series GC. The name of the new instrument remains GC3 to accommodate for the post run macros that use the GC3 name in the data handling and transfer to Janus.

The new GC3 was plumbed with copper tubing directly from the back of the instrument to the already existing regulators on the back "wall".

The regulators pressures are set up as follows:

He supply at bottle: 105psi

He supply at regulator: 90psi

Air supply (Jun-Air) at regulator: 55psi

H₂ supply at regulator: 23psi.

There are no S-traps or chemical traps in line as in the case of the HP 5890 GC. The small 12" molecular sieve trap on top of the 6890 GC seems to replace the S traps.

GC3 is now configured with a 8' 1/8" HaySep "R" packed column coated with 80/100 mesh. The injection is done via a 1/16" Valco union connected to a Valco-to-Luer lock syringe adaptor. This injector connects to a 10-port Valco valve which is switched pneumatically by a Digital Valve Interface (no more HP actuator) hooked up to ship's air (via clear plastic tubing connected to green one). Samples are introduced via a 0.25cc sample loop connected to the Valco valve. The Valco valve (Valve 5) can be switched to backflush the column (OFF position). GC3 is equipped with an EPC to control flow to the purged packed inlet. Hydrocarbon separation is detected by an FID (FID1A as Signal 1).

The HP ChemStation used to run the new GC3 is still Version 5.04. Version 6 was not installed because of potential licensing problems encountered at each new install. Version 6.0 also does not provide any useful feature that warrants us wasting our time learning again a new version of HP ChemStation. In the HP Configuration, GC3 is configured as Instrument 2 with an HPIB address of 10. A new GC3 directory was set up with Methods, Data, and Sequence subdirectories while the old GC3 directory was renamed GC3_OLD and archived both on the C:\ drive of PC113 and in the Chem Lab folder on the new TECH Volume.

All post run macros necessary for Janus data transfer are located in the CORE subdirectory of the HPCHEM directory (those for NGA too).

The GC3 method in use is GC3_185.M with a run time of 13.65mn. Operating conditions are as follows:

Injector Temperature: 120°C;

Total Flow: 30.5ml/mn;

Column Flow: 30 ml/mn, Constant Mode selected;

Initial Oven Temperature: 120°C, hold time of 3.60mn;

Oven Ramping: 30°C/mn to 140°C (hold for 0.80mn), 30°C/mn to 120°C (hold for 3.20mn), 28°C/mn to 140 (hold for 4mn);

Detector Temperature: 250°C;

FID signal reads around 7 to 8;

Hydrogen Flow: 40ml/mn;

Air Flow: 400ml/mn;

No Make Up gas;

Valve 5 turned ON at 0.01mn, OFF at 7mn

The GC3 calibration was performed at the beginning of the Leg for standards A, B, C, D, 30%, 50% and 70%.

How to run Headspace Samples:

After the headspace has been in the oven for 30 minutes, remove the vial and prepare to inject the sample in either the GC3 or NGA gas chromatographs.

Toggle between the different open programs; GC3 (online), NGA (online), ODP - Chemistry application (JANUS) at the command bar to access these 3 programs.

The overall sequence for the operation would be to set up the correct sample number, run the headspace sample on either the GC3 or NGA, look at the chromatographic trace and correct it if necessary, make a report file and place this file into the JANUS database..

GC3:

Make sure you are in the Method and Run Control window. In the upper menu, select Run Control. Select Sample Info. This will bring up the screen to enter the sample and file names

Two things to do:

1. Change the Filename (Signal 1) to the appropriate name;
ie. "IH5HS.D" (use either H or X depending on coring technique)
2. Change the Comment to the same name as the sample ID;
ie. "1751075A/IH5W0.0-5.0HS"

Then hit OK

These numbers and letters represent the Leg (175), the Site and Hole (1075A), the Core and Section (1H5), the Working Half (W), the Sampled Interval (0.0 - 5.0 cm), and the type of sample (HS or VAC).

Inject 5 ml of headspace while keeping the flow control between 30 and 40 units and hit the START button on the GC.

When the GC run is done the analysis must be checked for accuracy. First check your numbers on the screen printout, then CLOSE the printout and go to the View menu and select Data Analysis to look at the GC trace. The only buttons you should click on are: 1) the zoom in and out button to enlarge or reduce a chosen chromatogram, 2) the X button to delete a chosen peak area integration information, 3) to integral button to reintegrate a peak area use the mouse and draw a new baseline, when you release the mouse, the peak is automatically integrated, and the 4) split peak button used to split double peak at the valley.

After correcting the chromatogram hit Report and Print Report.

From the prepared report you will need to manually write down the values for C1 to C3 on the clipboard. At a later date you will need to add these values to the program on the Mac at the desk so that you will have a file of headspace data to work with at your leisure.

The data is now ready to be sent to the JANUS Database, select Janus on the command bar. (see JANUS section for directions).

NGA Setup

Dan:

Refresh my memory. Unfortunately I did not bring out my notes from our discussion about what was needed initially to buy from HP to plumb the TCD/FID GC. We may have discussed this but I don't have my notes out here on the ship off the coast of Japan.

1) The back inlet controls the temperature of the heater for the HayeSep R(AW) column. The front inlet does not appear to have the ability to control temperature. The two inlets look exactly the same (PCM), yet one can control temp and one cannot (there is a not a temp field on the display). There is not a temperature associated with it. Although we don't need the temp ability should the front inlet be able to control temperatures?

2) This is probably an HP question. Why can we plot the variables associated a cap column but not a packed column? Example, I can ramp the flow for both a capillary and a packed column, but the plot capability will only plot the changes in flow for the capillary column but be "greyed out" for a packed column.

3) There is a mystery peak that elutes between the ethanes and the propanes on the HaeySep R(AW) column. Normally, this is where H₂S and/or water elutes. This mystery peak completely obscures anything else that would elute at this time. There should not be any water (moisture) in the standards and we've never had a water peak with the HP 5890 GC you plumbed for us 10 years ago. If we bake out the HayeSep R(AW) column, it will go away for one sample (suppose I just should an air sample).

By the next sample it is back. The chei lab is an air conditioned lab and the humidity is no more than 72%.

The lab conditions are the same conditions with the 5890. Any ideas?

How do we get rid of it?

4) About the Inlet, why is there a septum purge, since we are not using the split/splitless function (packed column).

5) How do we program the Chemstation to recognize columns that are joined together. I.e. There is a description of the columns that the software uses to figure out flows. How do you put in columns that are joined together, a 3' molsieve attached to a 6" Poropak T.

Leg 185 NGA Set Up Summary

NGA, a 5890 Series II Plus GC, was replaced this Leg by an new HP 6890 Series GC. The name of the new instrument remains NGA.

The new NGA was plumbed with stainless steel tubing directly from the back of the instrument to the already existing regulators on the back "wall".

The regulators pressures are set up as follows:

He supply at bottle: 105psi

He supply at regulator: 92psi

Air supply (June Air) at regulator: 56psi

H₂ supply at regulator: 23psi.

NGA is configured as a multi-valve and multi-column GC. It is equipped with both a TCD (TCD1B as Signal 1) and an FID (FID2A as Signal 2).

A multiple Valco valving system is used to direct flows to the different columns and sample loops. Valve 1, 3, and 4 are on the top of the GC, valve 2 is on the left side of the GC. They are all actuated with DVIs hooked up to ship's air.

The little box on the right side of the NGA (BRIC 24 4C Hamlin) replaces the INTEG D3C 19405B Event Controller.

The multi column system as described on the Booker diagram includes:

- a SGE 50QC3 BP-1 capillary column with dimensions of 60m x 0.32mm (ID) x 0.1 um (film thickness).
- a 6" stainless steel column packed with Poropak T (50/80 mesh) in line with a 3' column packed with Molecular Sieve 13X (60/80 mesh); and
- a 6' stainless steel column packed with HaySep R (80/100 mesh);

The injection is done via a 1/16" Valco union connected to a Valco-to-Luer lock syringe adaptor. This injector connects to the 6-port Valco valve (V1) switched pneumatically by the GSV DVI. When V1 is in the Load (OFF) position, samples will be introduced onto the columns via three sample loops (0.25cc, 1cc, and 0.5 cc). When V1 is in the Inject position (ON), the sample will be loaded onto the capillary column for separation of C1 to C7. Valve 2 (V2) is a 4-port Valco valve that can be switched (using the CAP BF VLV DVI) to backflush the capillary column (OFF position). Valve 3 (V3) is an 8-port Valco valve connected to a 1 cc sample loop and the Haysep R column which is used to separate air and methane from CO₂, ethylene, ethane, H₂S, propylene and propane. After Propane has eluted, V3 is switched OFF (using the 6FT HSI(RAW) DVI) to backflush the Haysep column. Valve 4 (V4) is a 10-port Valco valve connected to a 0.5 cc sample loop and the Poropak T and Molecular Sieve columns that are used to separate N₂, O₂, methane and CO. Valve 4 is switched OFF (using the Col T x13 DVI) immediately after V3 is opened to backflush the columns.

Thermal AUX 1 is the heated zone for Valve 1 and 4 with a recommend temperature of 110°C (max 175°C). Thermal AUX 2 is the heated zone for Valve 3 with a recommend temperature of 110°C (max 175°C). The Back Inlet heated zone, where the Haysep R column is located, has a recommended maximum temperature of 80°C. AUX 3 functions as an EPC for flow into capillary column with a recommend setting of 15 psi. AUX 4 functions as an ON/OFF switch for the He purge (refer to Chieh's email on NGA).

In the HP Configuration, NGA is configured as Instrument 1 with an HPIB address of 5. A new NGA directory was set up with Methods, Data, and Sequence subdirectories while the old NGA directory was renamed NGA_OLD and archived both on the C:\ drive of PC113 and in the Chem Lab folder on the TECH Volume.

The NGA method was not fully developed this Leg. 185_3.m is the method currently loaded in memory. Run time is 16mn. A lot of parameters were set based on Dan Aiken's method 3 (March 23, 1999) stored in the GC (see GC1 Book #3 for copy of Dan's parameters). The 185_3.m method parameters are set as follows:

• Column 1 -- Capillary Column

- Front Inlet Pressure: 12.5 psi;
Column Flow: 1.5 ml/mn, Constant Mode selected;
Initial Oven Temperature: 40°C, hold time of 10mn;
- Oven Ramping: 10°C/mn to 100°C, no hold;
Front Detector Temperature: 250°C;

FID signal reads around 7 to 8;
Hydrogen Flow: 40ml/mn;
Air Flow: 400ml/mn;
Make Up gas: 50 ml/mn;
AUX1 OFF;
AUX 3 set at 13 psi;
AUX 4 OFF.

Note: Dan Aiken's methods recorded in the 6890 GC memory show capillary column dimension of 30m x 0.320mm ID. The column in place was not calibrated because we are not exactly sure of its true dimensions. AUX1 is set at 50°C in Dan Aiken's method but it has been turned off as the actual value is 65°C.

• Column 2 -- Packed Columns

- Back Inlet Temperature : 80°C;
Column Flow: 30 ml/mn, Constant Mode selected;
Initial Oven Temperature: 40°C, hold time of 10mn;
Oven Ramping: 10°C/mn to 100°C, no hold;
Back Detector Temperature: 150°C;
TCD signal reads around 30 to 40;
Reference Flow: 30ml/mn;
Make Up gas: 0 ml/mn;

• Run Time Table

- At 0.01 mn, valve 4 is turned ON;
At 0.07 mn, valve 1 is turned ON;
At 0.08 mn, valve 2 is turned ON;
At 2.00 mn, valve 3 is turned ON;
At 2.06 mn, valve 4 is turned OFF;
At 11.00 mn, valve 3 is turned OFF;
At 11.00 mn, valve 1 is turned OFF;
At 11.01 mn, valve 2 is turned OFF.

Notes:

- HP ChemStation requires that the operator defines the column parameters (type and dimensions) at installation. Since the contraction of the three packed columns cannot be defined in the software, the inlet is flow-controlled only, i.e. you can only select two modes for the column: constant flow and ramp flow. That is why the column flow was set to 30ml/mn and a constant flow mode selected.

The TCD signal is very high compared to the signal value of the TCD on the 5890 GC (1.5). We cannot find a way, in the software or the hardware, to set low and high sensitivities for the TCD like we use to be able to on the 5890 GC. The HP on-line help of the 6890 GC seems to indicate that sensitivity is linked to filament temperature. Between 150°C to 200°C, the filament is at low setting, above 200°C, the filament is at high setting, or whatever that means!

A few standards were injected using 185_3.m. Examples of FID and TCD chromatograms for both the 185_3.m method used on the 6890 GC and the TCD184.m method used with the 5890 GC are stored for comparison in the NGA three ring binder.

The chromatography for the TCD on the 6890 GC is not very good. Peaks in general are not well separated and are tailing. Because the sensitivities cannot be adjusted to high, C2=, C2, C3=, C3 are very

small compared to the O₂, N₂, C₁ and air peaks. Also C₃= and C₃ elute as one peak?

The chromatography for the FID on the 6890 is better but definitively can use some improvement. Separation between C₁ and C₂ is poor. There is no separation between C₂= and C₂, and between C₃= and C₃. If working on the chromatography does not improve the separation, we suggest to install the spare J&W DB-1 column stored above the GC/MSD.

Notes:

The FID flame goes OFF when valve V1 switches;

For some annoying reason, HP ChemStation has assigned FID 2A to the FID signal and TCD 1B to the TCD for the 6890 GC. FID 2B and TCD 1A used to be the signal assignments for the 5890 GC. The calibration table does not adjust for these signal changes, therefore a new calibration table will have to be designed from scratch once you have the final methodology figured out.

Performing a Recalibration Using HP ChemStation v.179

At the beginning of each Leg and prior to arriving at the first site, GC3 and NGA have to be recalibrated. Calibration is done using the HP ChemStation (HP Chem) by injecting standards of increasing concentrations into the GCs.

The first step to perform before actually starting the calibration is the set up the various GC3 and NGA directories (methods and data) that will be used for the specific Leg. To set up the HP ChemStation directories for the GC3 and NGA, proceed as follows:

- Double click on the "HPChem Directory" icon on the desktop, and select either the NGA or the GC3 directory. In both their Data and Methods directories, create a Leg directory (Leg 179 for example). Copy the last method file (i.e., folder.m) used in the previous Leg in the Methods directories. Then double click on the "HP Configuration Editor" icon on the desktop (all HP Chem sessions have to be closed for the Editor to open), and select Path under the Configure menu. To the usual Data and Method path, add the Leg directory. For example, the data directory path for the GC3 on Leg 179 will read: C:\hpchem\GC3\data\leg179, the method directory path for the GC3 will read C:\hpchem\GC3\methods\leg179. Make sure you save the new configuration under the File menu.

Start GC3 and NGA by double clicking on the "Online" icons for each instrument. Go to the Method Menu (in Method and Run Control window) and load the last method used. In the case of GC3 for example, load GC3_178.m (from the subdirectory Leg 179), save it as GC3_179.m. Use that new method to recalibrate GC3. Before you start the recalibration create a standard subdirectory (CALIB) in the Sample Info window (under the Run Control menu in the Method and Run Control window), where all the standards runs will be stored. Also, for each site you can create a site (and then a calib) subdirectory in the Sample Info window.

1. Calibrating GC3

The following standards are usually used to calibrate GC3: A, B, C, D, B3-3, 30%, 50%, 70% and 99%. The calibration can be done with a few or all standards, but in any case it should be performed with a minimum of two standards. The concentrations for these gases are listed on the "Multi Component Gas" table hooked to the shelf above the HP Chem computer.

To explain how to perform a (re)calibration, we will use the example of the Leg 179 calibration.

Before starting the (re)calibration, print the old calibration in the method you have just renamed. To do so, select Print Method under the Method Menu and select Calibration Data in the Data Analysis box and click on Print. Selecting the Check All button will print the entire method. Printout 1 shows the old 178 calibration table. It gives additional information such as the last calibration modification date (which does not imply last recalibration date), quantification mode (ESTD based on peak area), absolute and relative values for reference and non-reference windows, curve fitting type (usually piecewise), and origin treatment (usually included in response curve), etc.

We will use the example of level 1 to illustrate the recalibration of a particular level. Note that each level in the calibration table represents a specific standard. In printout 1, Level 1 represents standard A, level 2--standard B, level 3--standard C, level 4--standard D, level 5--standard 30%, level 6--standard 50%, and level 7--standard 70%. Also, HP Chem assigns a unique peak number to each peak (i.e., component) in the calibration table in order of elution. Peak 1 measures Methane (C₁), peak 2--Ethylene (C₂=), peak 3--Ethane (C₂), peak 4--Propylene (C₃=), and peak 5--Propane (C₃). The peak # are not displayed in the printout for some reason.

To recalibrate any level, we inject three times the standard of interest. To recalibrate a level (level 1--standard A-- in this example), proceed as follows:

Under the Run Control menu (in Method and Run Control window), select Sample Info and specify the filename for the run in the Signal 1 box (STDA1, STDA2 etc.). Do not change the Sample Parameters and do not enter a Comment. Inject the standard A three times. After each run, print the report. HP Chem will automatically display the report on the screen at the end of each run. To print this report, select Print at the bottom right of the screen and then close the report;

Examine both the area counts and concentrations of the three run for a particular standard to check if the runs are reproducible and to see how close the concentrations obtained in the three runs are to the theoretical concentrations listed on the "Multi Component Gas" table. If the area counts and concentration values are not consistent from one run to the other, keep injecting the standard till you have good reproducibility. A reproducibility and accuracy of 5% are acceptable but ideally the accuracy should be 2%. If the accuracy and reproducibility are higher than 5%, the instrument needs to be recalibrated for that particular standard. Printout 2 shows the reports of the three runs for standard A (level 1). The Reproducibility is acceptable but accuracy is way over 10%, GC3 needs to be recalibrated for level 1. Usually if one level is uncalibrated, there is a great likelihood that all levels need recalibration;

Load one of the three data files for level 1. To do so, go to the View menu and select Data Analysis. This will change the Method and Run Control window to the Data Analysis window with an all new set of menus. Under the File menu, select Load Signal. From the scrolling table, select one data file for level 1, STDA2.D for example. From the Calibration menu, select Recalibrate. This option will be used to update the existing calibration table. In the message box that appears, select Replace. The existing calibration data is subsequently replaced by the new calibration data. Be sure to specify the level for which you want to update the data in the existing calibration table. In this example, enter 1 and click OK. The software will ask you whether to save the updated calibration table to the current method, select Yes. A calibration report is prompted on the screen, close it. Then print a report for the standard you just recalibrated. Under Report, select Print Report to print on the screen. All the concentrations for that standard (STDA2) should now be equal to the theoretical concentrations;

Load one of the other two standards you run for level 1 (STDA1.D for example). The run is automatically integrated by HP Chem but you should always check the software's integration and be prepared to manually reintegrate it. Selecting Print Report under Report will prompt the report of the reintegrated run on the screen. To actually print the report, select Print at the bottom right of the window. Printout 3 shows the report for STDA1 after replacing the calibration data in the calibration table using

STDA2. If the concentration values are very close to the theoretical values (as shown on printout 3), go to the Calibration Menu and select Recalibrate. This time select Average in the Recalibrate box for level 1, and click on OK. New calibration data is then averaged with the existing calibration data. Again print a report for STDA1 to see how close the new concentrations are to the theoretical values (see Printout 4);

Load the remaining standard run (STDA3.D) and proceed as described in the above paragraph;

Recalibrate all other levels if necessary in the same way you did level 1;

View the calibration curve of each peak (component) in the calibration table to make sure your calibration is good (in case of GC3, it should be linear). To do so, select Calibration Table from the Calibration menu (or click on the Calibration tool which looks like a balance) . The calibration table is displayed with the calibration plots located on the right window. You can view a particular peak's calibration curve by highlighting that particular peak in the table. You can zoom/unzoom portion of the curve using the cursor;

Save the method with the updated calibration table (GC3_179.m). Using View, go back to the Method and Run Control window, and under Method, select Save Method, then Print Method to send it to the printer (Printout 5).

2. Calibrating the NGA

The first step before starting the calibration of the NGA is to print the old calibration table included in the NGA method. One method is used to run the equipment with one calibration table but in fact the NGA calibration will involve two calibrations: an FID calibration and a TCD calibration. Because the NGA has two detectors (TCD and FID), there are two signals acquiring data (Signal 1 and Signal 2). Signal 1 on the instrument refers to the TCD and Signal 2 refers to the FID. In the calibration table screen of HP Chem, when a peak was provided by a particular signal, it will be labelled appropriately with either FID2 B or TCD1 A. However, when the calibration table is printed, #1 and #2 replace the signal denomination. CAREFUL!! On the printout Sig 1 will now refer to the FID2 B signal and Sig 2 to the TCD1 A signal. See printout 6.

The following standards are usually used to calibrate the NGA: B, C, D, B3-3, 30%, 50%, 70% and 99%. As with GC3, to recalibrate any level, we inject three times (minimum) the standard of interest. Make sure you specify a filename for each run in the Sample Info menu. There is only one file name for both Signal 1 and Signal 2. We usually perform the FID calibration first.

2.1. FID Calibration

The DB1 capillary column in the NGA is used to separate small quantities of C₁ through C₃ hydrocarbons and any quantity of C₄ to C₁₀ hydrocarbons. These hydrocarbons are detected by the FID detector whose signal is integrated by HP ChemStation.

For recalibrating a level, proceed as follows:

In the Data Analysis window, select Load Data File under the File Menu. In the Load Data window, select the option Full so you can see the file name and the signal information windows. Select the three files referring to the 3 runs for one particular level (STDD1R.D, STDD2R.D and STDD3R.D for example) and each time you load a particular file, select also FID2 B in the signal window. Print the reports;

Examine both the area counts and concentrations of the three run for a particular standard to check for reproducibility and accuracy. If the accuracy and reproducibility are higher than 5%, the instrument needs

to be recalibrated for that particular standard. Often, some calibrated peaks will not be found by the software. This is a frequent occurrence when running samples with the NGA. The software has difficulties integrating two groups of peaks (C₁-C₂-C₂₌ and C₃-C₃₌) because these peaks have close retention times. These peaks have to be reintegrated manually.

Let's take the example of the old 178 calibration to show how to perform a manual reintegration. The peaks C₁, C₂ and C₂₌ have close retention times (3.026, 3.075 and 3.101 in printout 6) and often the C₂, C₂₌ components elute as a bimodal peak that has to be manually separated.

To reintegrate these three peaks manually, using the integration tool bar (obtained by clicking on the Integration button that looks like a Integral sign) proceed as follows:

Click on the Zoom In (magnifying glass with a plus sign) button to magnify the portion of the chromatogram containing the three peaks. Then click on the Delete Peak button (button at the extreme right of the tool bar with a red X) to delete the peak from the integration results. You can delete individual peaks by clicking on each independently or you can delete all three at a time by drawing a rectangle around the three peaks to be deleted. When you click the mouse, the retention time and baseline will be gone;

Click on the Manual Integration button (the first one to the right of the white arrow) and redraw the baseline of the three peaks as you think they should be integrated. To redraw a baseline, press the left mouse button at the beginning of the peak and then move the mouse to the endpoint of the peak. A rubber band line anchored at the first point will follow the cursor to graphically show the location of the baseline. Releasing the left mouse button will reintegrate the peak;

For the bimodal peak that needs to be separated (C₂-C₂₌ peak), after you have redrawn the baseline for that bimodal peak, click on the Split Peak button (the one directly to the left of the Delete Peak button). With the cursor, pick the spot (bottom of valley) where you want to split the peak. When you click the left mouse button, a dropline will split the peak into two peaks which are then automatically integrated.

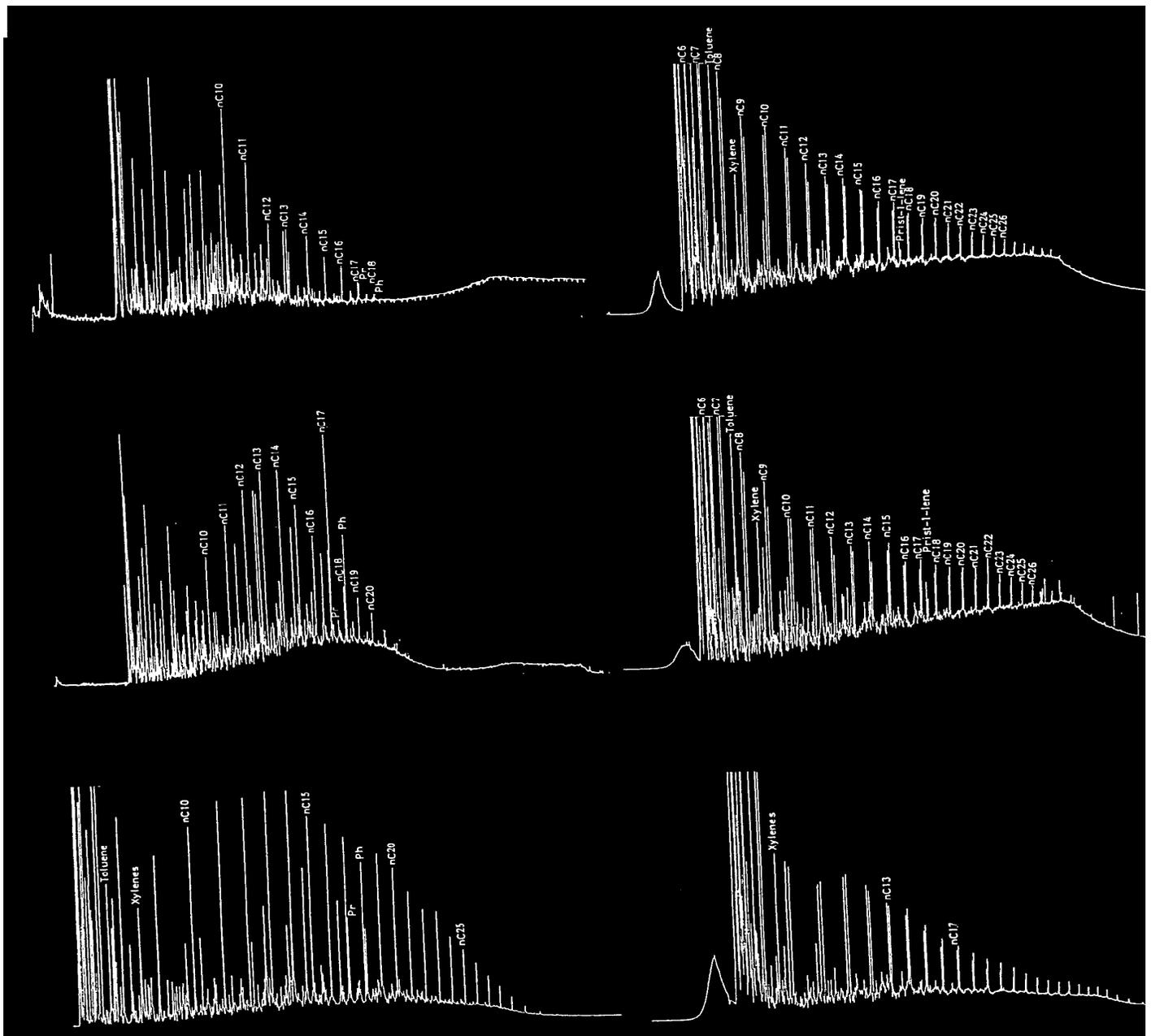
The HP Chemstation does not save your manual integration, that is why once you have manually reintegrated one of the standard run, you have to update the calibration table immediately with that run. Proceed from there on as described above for GC3.

2.2. TCD Calibration

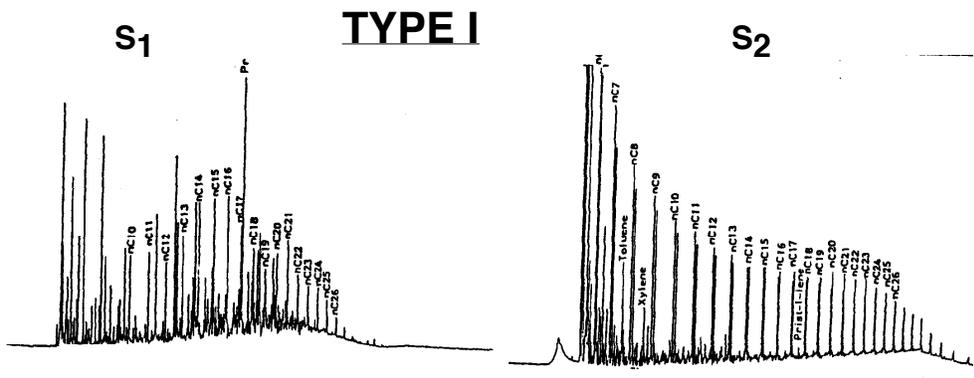
The TCD will detect O₂, N₂, C₁, CO₂, C₂, C₂₌, H₂S, C₃ and C₃₌. To calibrate the TCD, you proceed as described in the FID calibration section.

In summary:

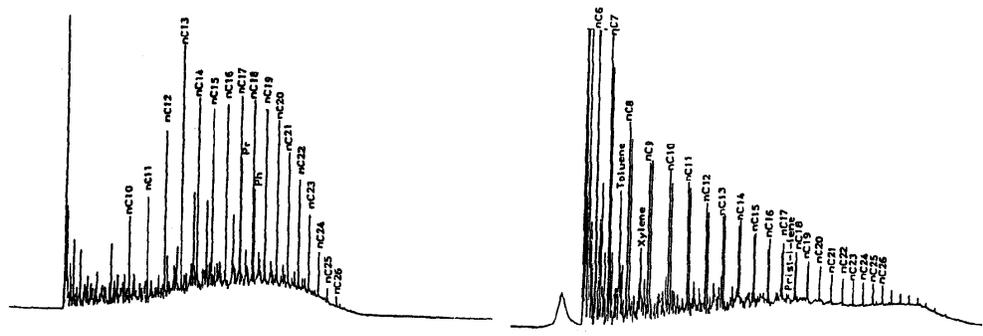
Load and print the three data files for the each standard while selecting the TCD1 A option;
Manually reintegrate where necessary (the software will often have trouble integrating O₂, N₂ and C₁);
Replace or Average the standard run using Recalibration under the Calibration Menu to update the TCD calibration table; and
Review the calibration curves. Save and Print the updated method with the new calibration table.



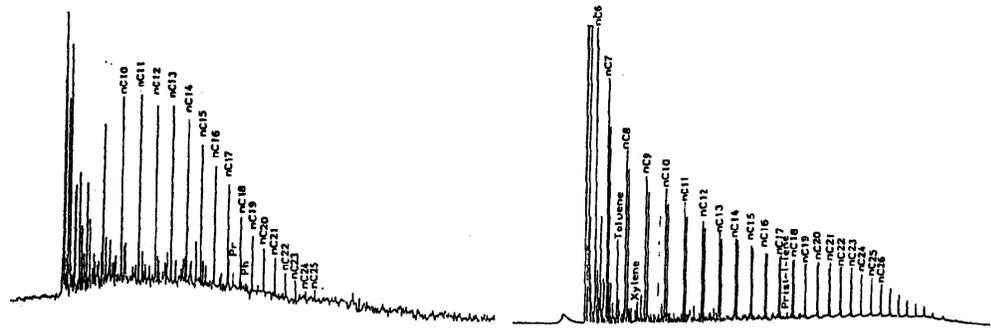
mature



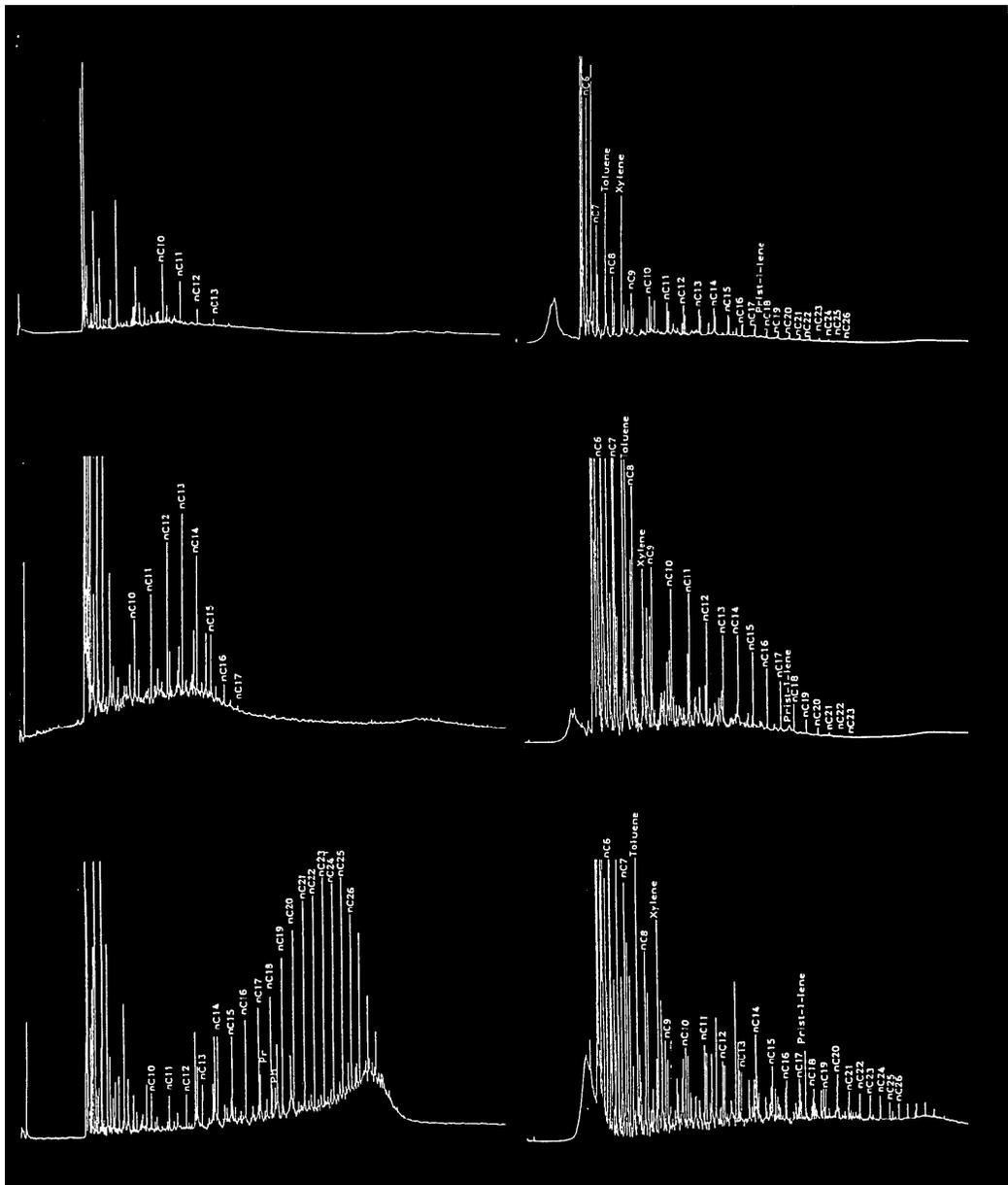
Immature



Semi Mature



Mature



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