EPA

US EPA Office of Research and Development

ICE* is Easy

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Detailed instructions for performing ICE with a Finnigan MAT 900 ion trap mass spectrometer with ICL 1 [illegible] system and an [illegible] vs NT.

*Ion Composition Elucidation

Mt. Hood, Oregon

Click

Acronyms

MPPSIRD – Mass Peak Profiling from Selected Ion Recording Data

PGM - Profile Generation Model

ICE is Nice, which is available from grange.andrew@epa.gov, describes MPPSIRD and the PGM, and illustrates applications of ICE. It should be viewed before **ICE is Easy**.

During this presentation:
right click to pause, then
left click to resume.

Numerous column labels contain "M+1" or "M+2". Fragment ions are also investigated using ICE. Ignore the "M" in these headers.

Click

Determining an Ion Composition

Select an ion in the low resolution mass spectrum

Acquire Survey Data

Acquire Full Profile with 10,000 Resolution

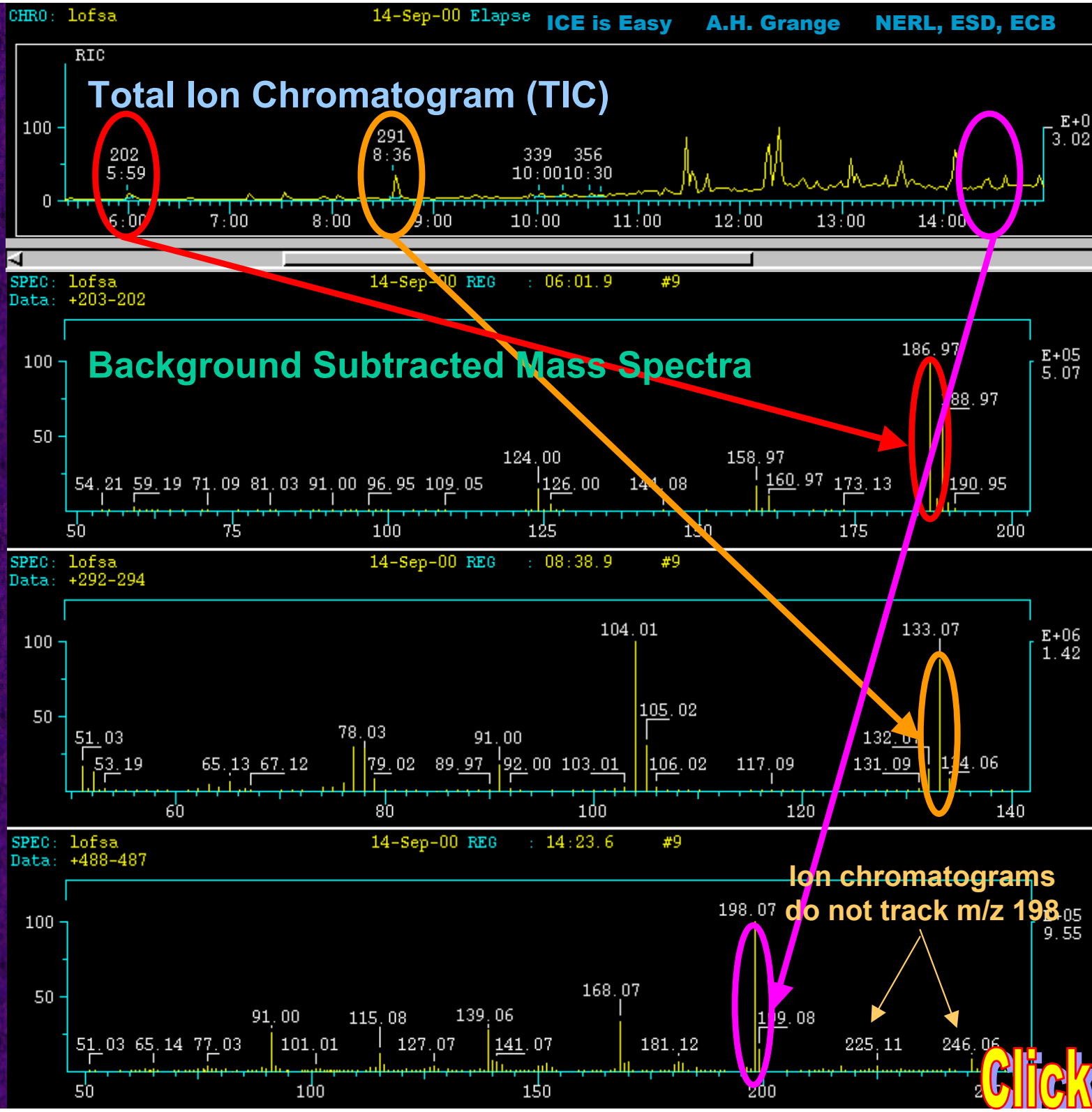
Enter Exact Mass into the PGM – Select Hypothetical Composition

Acquire Full or Partial Profile Data

Enter Exact Masses and Relative Abundances into the PGM

Click

Ion compositions will be determined for the apparent molecular ions from background subtracted mass spectra for 3 chromatographic peaks in the total ion chromatogram.



Prior Preparation ...

If MPPSIRD has not been performed recently, it is prudent to perform:

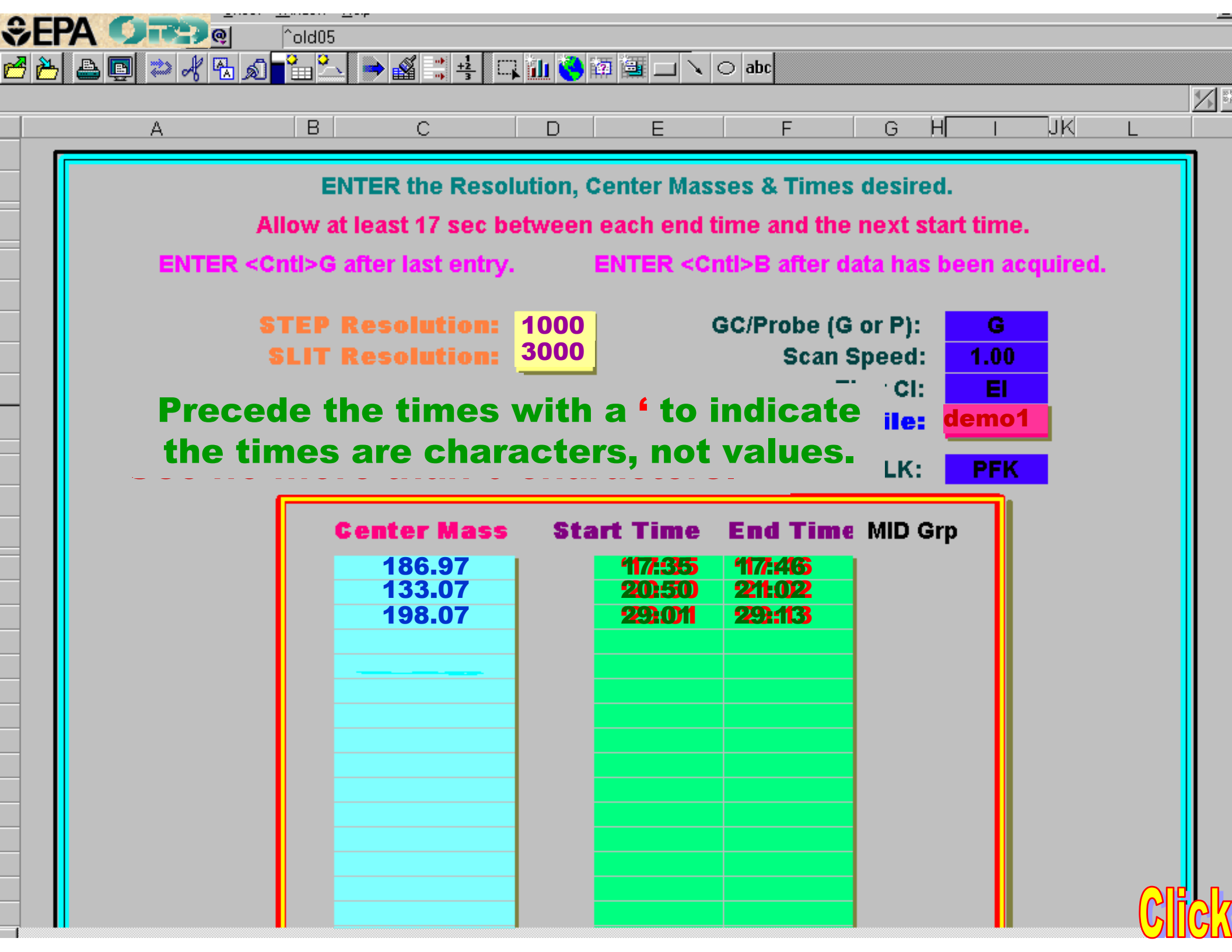
1. **A magnetic calibration using PFK over a mass range that includes at least 50 Da below and 100 Da above all masses to be studied.**
   .pfkcal 50,500,10,3

2. **An electric scan calibration**
   .aec

If lock-on fails, perform both calibrations. This generally solves the problem.

These procedures are described in screen 37.

Click


EPA
old05
ENTER the Resolution, Center Masses & Times desired.
Allow at least 17 sec between each end time and the next start time.
ENTER <Cntl>G after last entry.
ENTER <Cntl>B after data has been acquired.
STEP Resolution: 1000
SLIT Resolution: 3000
GC/Probe (G or P): G
Scan Speed: 1.00
CI: EI
ile: demo1
LK: PFK
Precede the times with a ‘ to indicate the times are characters, not values.
Center Mass
Start Time
End Time
MID Grp
186.97
133.07
198.07
17:35
20:50
29:01
17:46
21:02
29:13
Click

File Edit View Create Range Sheet Window Help

^demo1

ENTER the Resolution, Center Masses & Times desired.

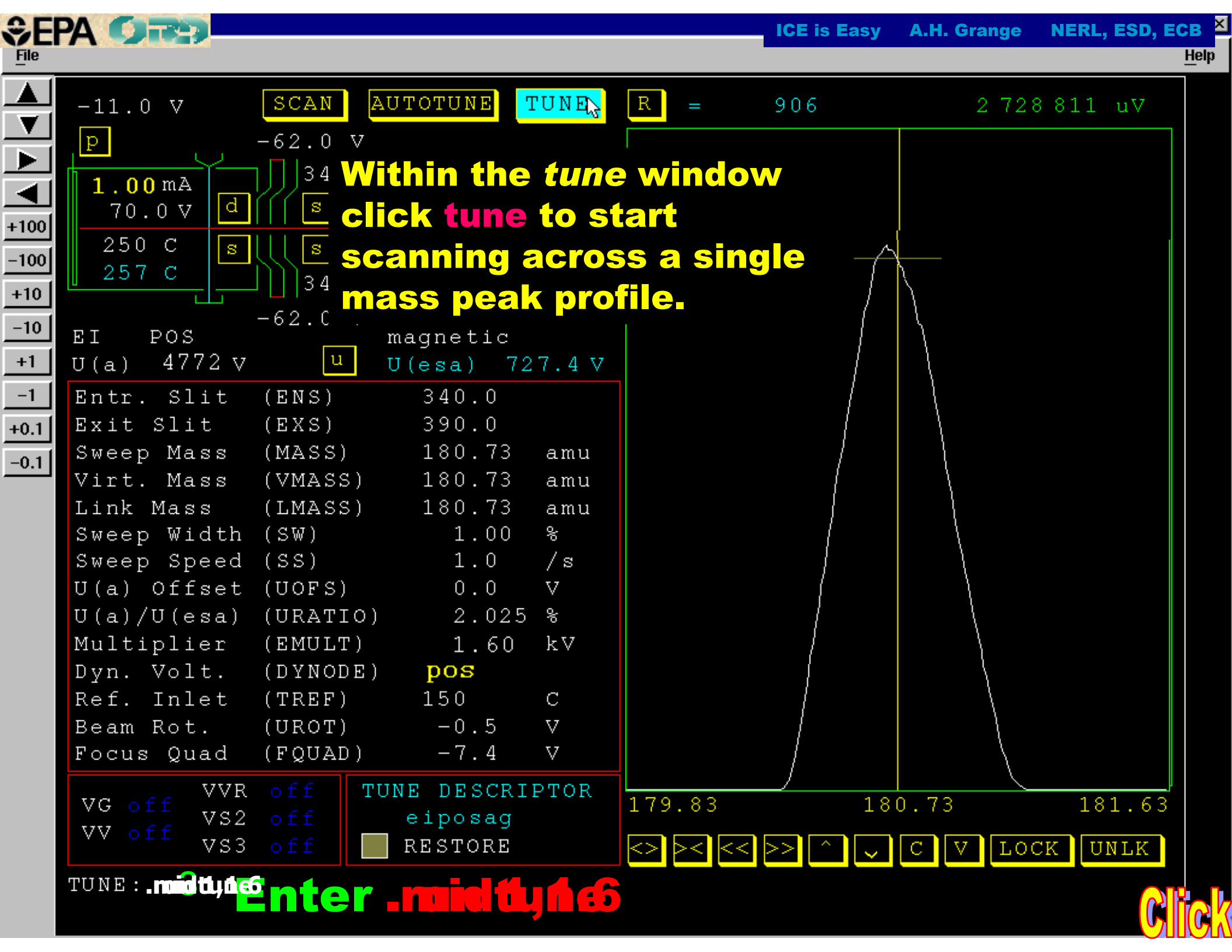
Allow at least 17 sec between each end time and the next start time.

ENTER <Cntl>G after last entry. ENTER <Cntl>B after data has been acquired.

STEP Resolution:	1000	GC/Probe (G or P):	G
SLIT Resolution:	3000	Scan Speed:	1.00
		EI or CI:	EI
3.3 pts/prof		Datafile:	demo1
5 5 ST ET 5		PFK or ALK:	PFK

Center Mass	Start Time	End Time	MID Grp
186.97000	17:32	17:44	
133.07000	20:50	21:02	
198.07000	28:55	29:07	

Click


EPA
ICE is Easy
A.H. Grange
NERL, ESD, ECB
File
Help
-11.0 V
SCAN
AUTOTUNE
TUNE
R = 906
2 728 811 uV
-62.0 V
1.00 mA
70.0 V
250 C
257 C
-62.0
Within the tune window click tune to start scanning across a single mass peak profile.
EI POS
U(a) 4772 V
magnetic
U(esa) 727.4 V
Entr. Slit (ENS) 340.0
Exit Slit (EXS) 390.0
Sweep Mass (MASS) 180.73 amu
Virt. Mass (VMASS) 180.73 amu
Link Mass (LMASS) 180.73 amu
Sweep Width (SW) 1.00 %
Sweep Speed (SS) 1.0 /s
U(a) Offset (UOFS) 0.0 V
U(a)/U(esa) (URATIO) 2.025 %
Multiplier (EMULT) 1.60 kV
Dyn. Volt. (DYNODE) pos
Ref. Inlet (TREF) 150 C
Beam Rot. (UROT) -0.5 V
Focus Quad (FQUAD) -7.4 V
VG off
VV off
VVR off
VS2 off
VS3 off
TUNE DESCRIPTOR
eiposag
RESTORE
179.83
180.73
181.63
LOCK
UNLK
TUNE:
Enter
Click

mat900

File Help

GC-LC Type: HP 6890 GC GC not ready IC < GC

GC Descriptor

On Display: gc37

In GC : gc37

vmake 1;.#gc
vsend;.#gc;.#sc150
doze4

GC elapsed time 0.0 Min.
GC run time 10.0 Min.
Stabilize time 0.0 Min.

Current GC Temperature

+100 −100 +10 −10 +1 −1 +0.1 −0.1

Injector A	Transfer Line	Column
250/ 250 C	300/ 301 C	150/ 150
Max = 300 C	Max = 300 C	Max = 310

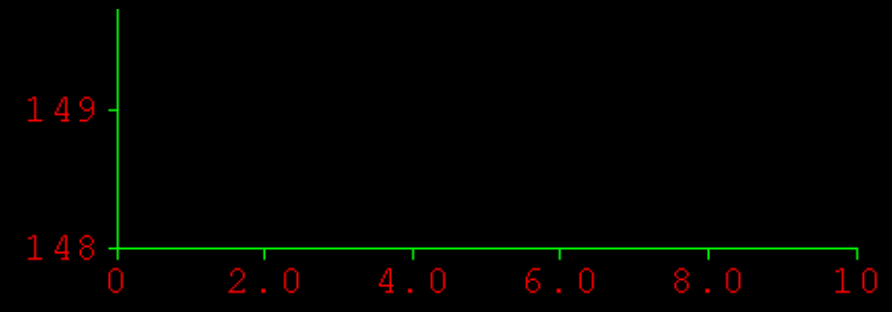
The column temperature is set to 150°C for *autotuning*. The ion source conditions are then more similar to those when analytes elute.

Column: Constant Flow 0.1 ml/min

Inlet: Splitless Mode

Purge time	Purge flow	Saver time	Saver flow
1.0	70.0	3.0	15.0

Saver



Sequence No. 1

Time Min 10

Rate C/Min

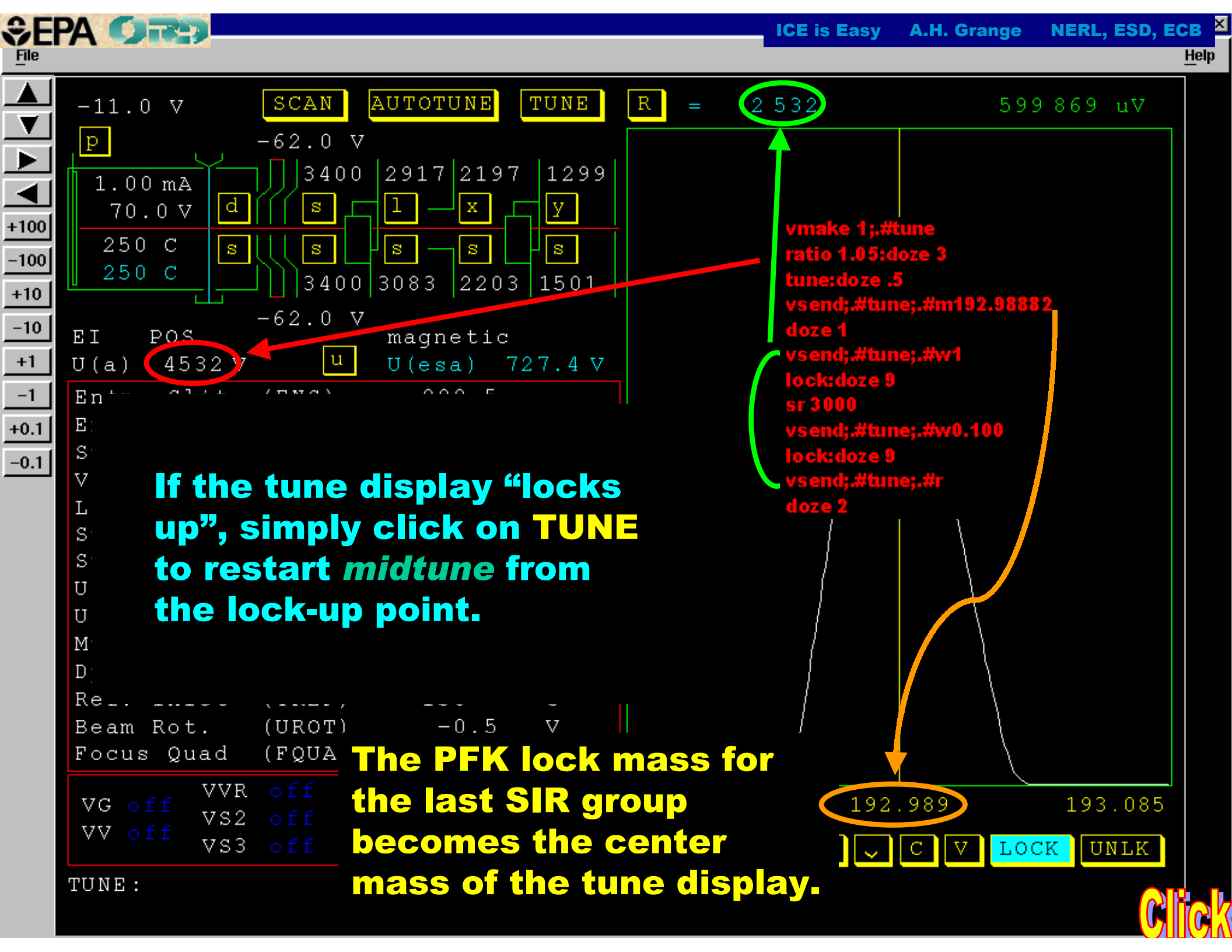
Temp. C 150 150

Total Time 0 10

START GC RESTORE LOAD CYCLE New Program

GC: _

Click


ICE is Easy
A.H. Grange
NERL, ESD, ECB
File
Help
-11.0 V
SCAN
AUTOTUNE
TUNE
R = 2 532
599 869 uV
-62.0 V
1.00 mA
70.0 V
250 C
250 C
3400 2917 2197 1299
3400 3083 2203 1501
-62.0 V
EI POS
U(a) 4532 V
magnetic
U(esa) 727.4 V
Beam Rot. (UROT) -0.5 V
Focus Quad (FQUA
VG off
VV off
VVR off
VS2 off
VS3 off
TUNE:
vmake 1;.#tune
ratio 1.05:doze 3
tune:doze .5
vsend;.#tune;.#m192.98882
doze 1
vsend;.#tune;.#w1
lock:doze 9
sr 3000
vsend;.#tune;.#w0.100
lock:doze 9
vsend;.#tune;.#r
doze 2
192.989
193.085
C
V
LOCK
UNLK
If the tune display “locks up”, simply click on TUNE to restart midtune from the lock-up point.
The PFK lock mass for the last SIR group becomes the center mass of the tune display.
Click

NOT ACQUIRING ELAPSED:

12 Jan 2001 10:31 END:

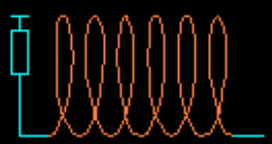
FILE:demo1 STUDY: Time: MID run time
SAMP:demo1 AMT: 0.00 VOL: 0.00
OPER: CLIENT: INJ.VOL: 1.00
COMM:Clark Co. effluent

+100 −100 +10 −10 +1 −1 +0.1 −0.1

START

METHOD LIST:
init(1)

SAVE

pm	gc37	mpp	mpp.icl	mid37
Vial 1				

< FILE > AUTOSAMP VIAL D:INLET ICL PROC. DS PROC. S/T/M DLY

demo1 pm 1 GC:gc37 simchr mpp.prn $ mid37

vmake 1;.#analysis
doze 2
vsend;.#analysis;.#f1^demo1^a^pm^v^1
vsend;.#analysis;.#g^gc37^i^simchr
vsend;.#analysis;.#d^mpp.icl $^m^mid37
doze 5

To run the correct GC temperature program, save the GC program desired as *GC37*.

ANALYSIS:

***The puzzle for running this program automatically has not been solved. Click**

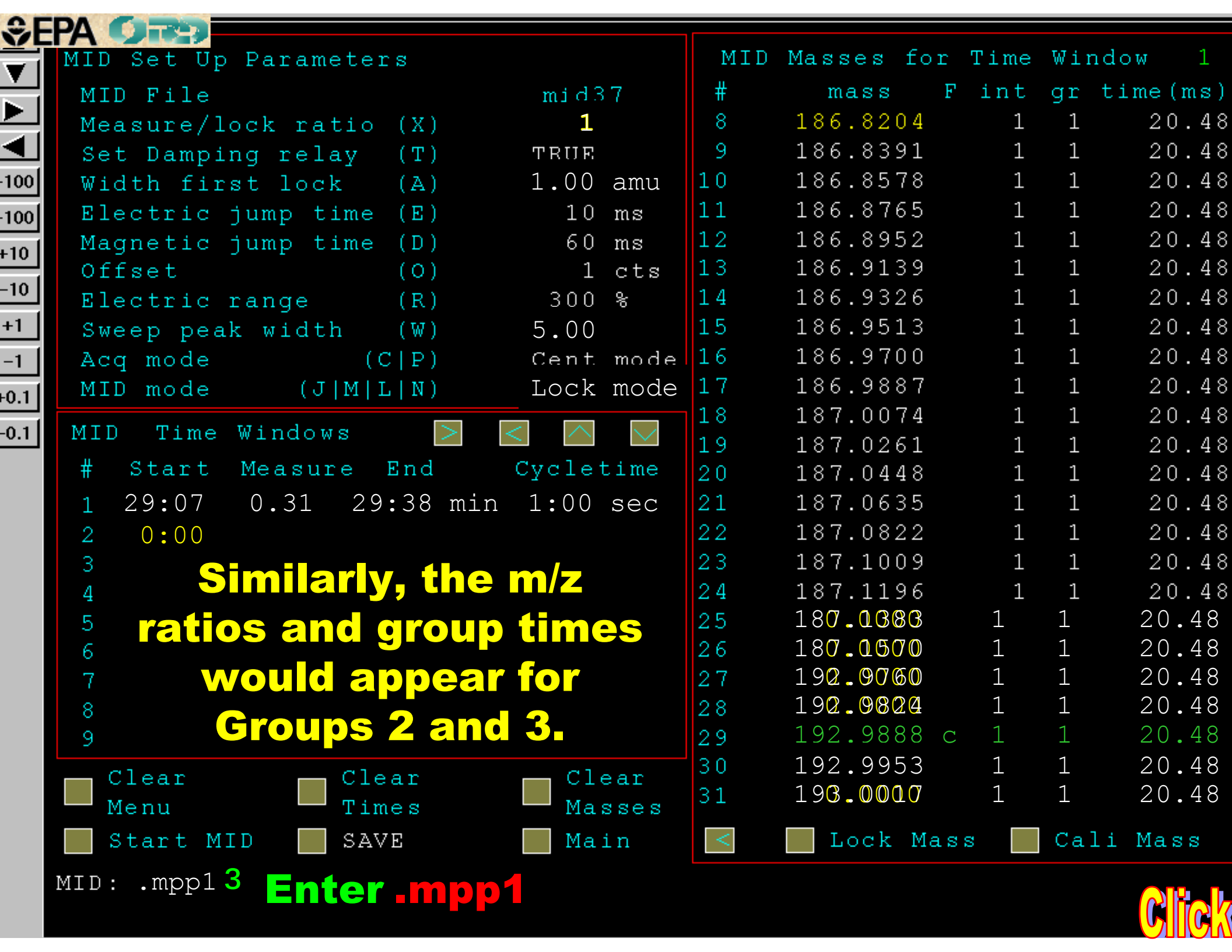
midtune.icl

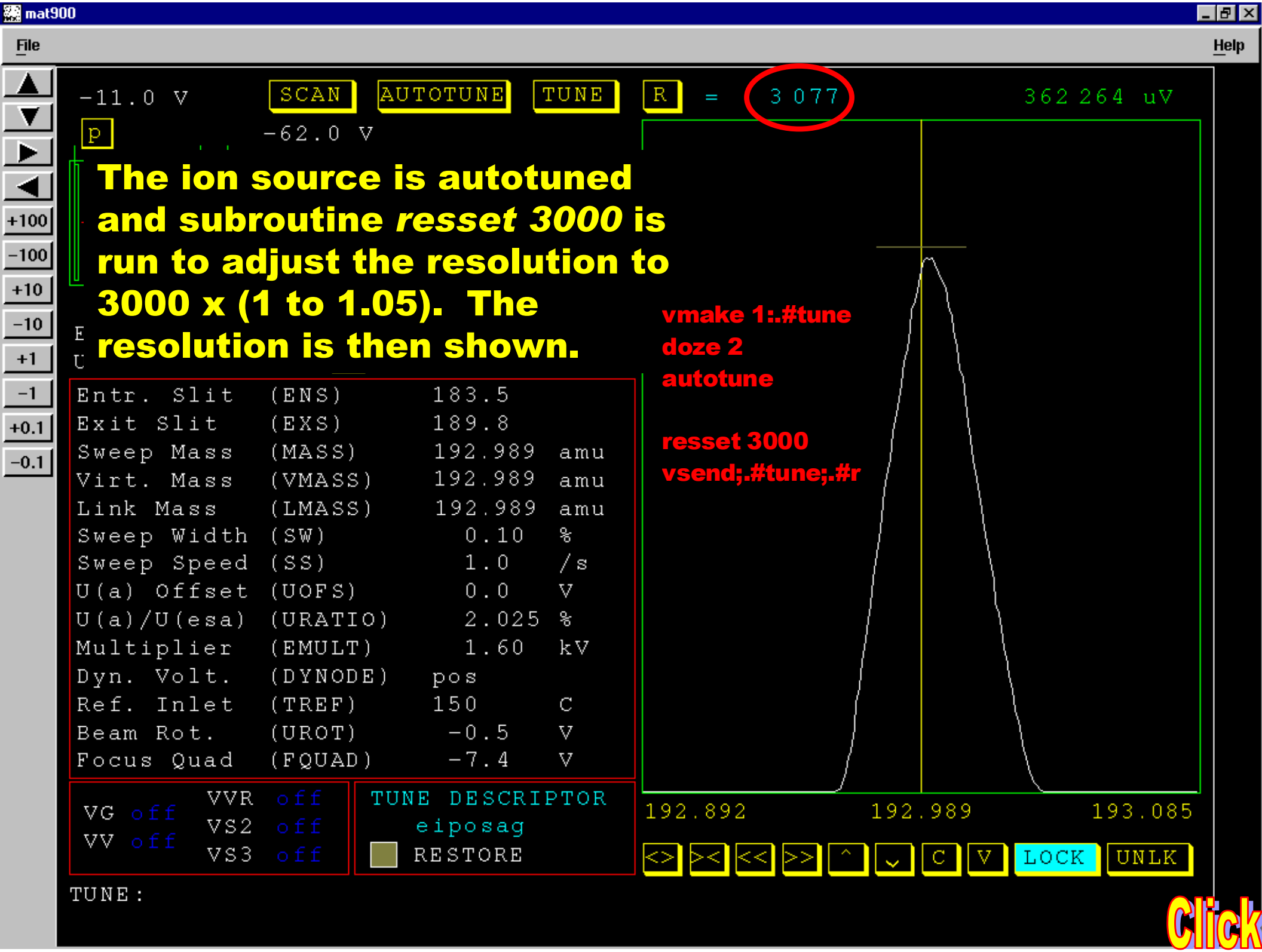
```
      :
      :
      :
vsend;.#analysis;.#d^mpp.icl^m^mid37
doze 5
vmake 1;.#mid
doze 2
mpp1
vmake 1;.#tune
doze 2
autotune


resset 3000
vsend;.#tune;.#r
vmake 4;.#tune;.#gc;.#mid;.#analysis
vsend;.#tune;.#w0.5
ratio 1
lock:doze 9
vsend;.#tune;.#w0.050
vsend;.#tune;#r
doze 1
vsend;.#gc;.#sc90
vmake 1;.#mid:doze 3
repeat 5
.#click >& enter mpp2, if > 9 groups
doze 1:.#
doze 1:end
vmake 4;.#tune;.#gc;.#mid;.#analysis
```

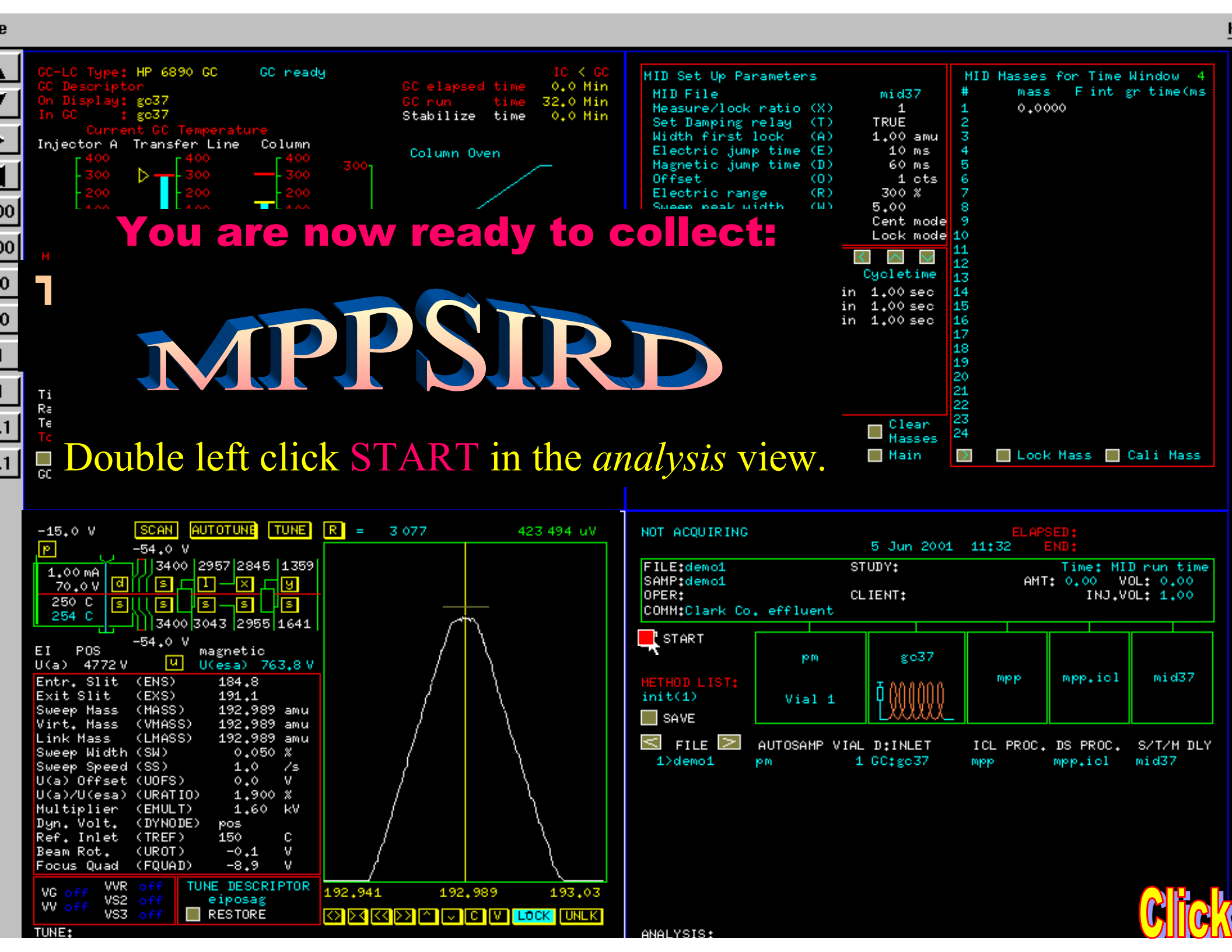
The *mid* view will appear and subroutine *mpp1.icl* will be run to prepare a SIR descriptor for each eluting GC peak.

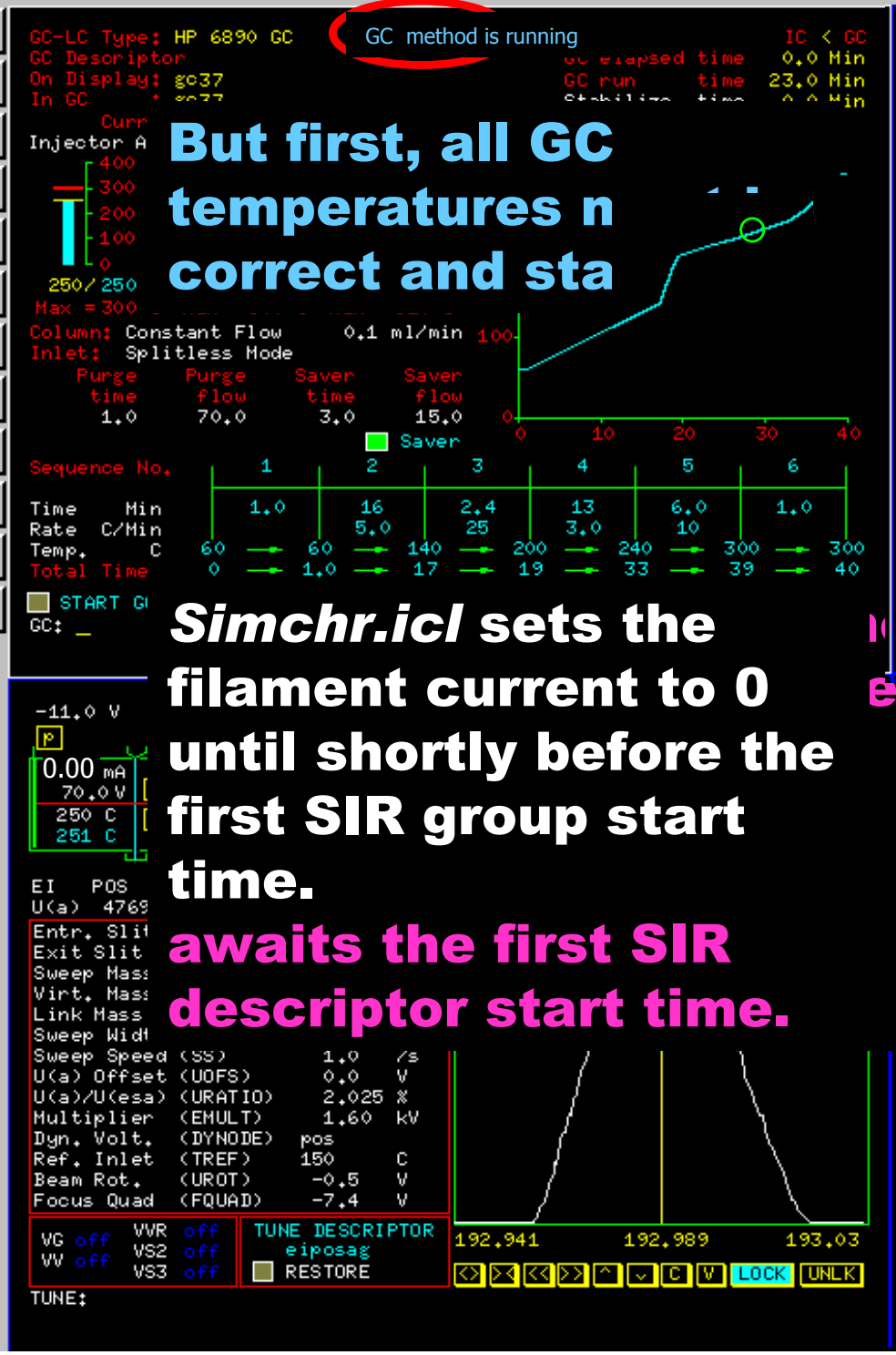
Note that subroutines such as *mpp1.icl* can be run independently of *midtune.icl*. This will be illustrated in the next screen.

Click


MID Set Up Parameters
MID File mid37
Measure/lock ratio (X) 1
Set Damping relay (T) TRUE
Width first lock (A) 1.00 amu
Electric jump time (E) 10 ms
Magnetic jump time (D) 60 ms
Offset (O) 1 cts
Electric range (R) 300 %
Sweep peak width (W) 5.00
Acq mode (C|P) Cent mode
MID mode (J|M|L|N) Lock mode
MID Time Windows
Start Measure End Cycletime
1 29:07 0.31 29:38 min 1:00 sec
2 0:00
Similarly, the m/z ratios and group times would appear for Groups 2 and 3.
MID Masses for Time Window 1
mass F int gr time(ms)
8 186.8204 1 1 20.48
9 186.8391 1 1 20.48
10 186.8578 1 1 20.48
11 186.8765 1 1 20.48
12 186.8952 1 1 20.48
13 186.9139 1 1 20.48
14 186.9326 1 1 20.48
15 186.9513 1 1 20.48
16 186.9700 1 1 20.48
17 186.9887 1 1 20.48
18 187.0074 1 1 20.48
19 187.0261 1 1 20.48
20 187.0448 1 1 20.48
21 187.0635 1 1 20.48
22 187.0822 1 1 20.48
23 187.1009 1 1 20.48
24 187.1196 1 1 20.48
25 1 1 20.48
26 1 1 20.48
27 1 1 20.48
28 1 1 20.48
29 192.9888 c 1 1 20.48
30 192.9953 1 1 20.48
31 1 1 20.48
Clear Menu
Clear Times
Clear Masses
Start MID
SAVE
Main
Lock Mass
Cali Mass
MID: .mpp1 3
Enter .mpp1
Click


mat900
File
Help
-11.0 V
SCAN
AUTOTUNE
TUNE
R = 3 077
362 264 uV
p
-62.0 V
The ion source is autotuned and subroutine resset 3000 is run to adjust the resolution to 3000 x (1 to 1.05). The resolution is then shown.
vmake 1:.#tune
doze 2
autotune
resset 3000
vsend;.#tune;.#r
+100
-100
+10
-10
+1
-1
+0.1
-0.1
Entr. Slit (ENS) 183.5
Exit Slit (EXS) 189.8
Sweep Mass (MASS) 192.989 amu
Virt. Mass (VMASS) 192.989 amu
Link Mass (LMASS) 192.989 amu
Sweep Width (SW) 0.10 %
Sweep Speed (SS) 1.0 /s
U(a) Offset (UOFS) 0.0 V
U(a)/U(esa) (URATIO) 2.025 %
Multiplier (EMULT) 1.60 kV
Dyn. Volt. (DYNODE) pos
Ref. Inlet (TREF) 150 C
Beam Rot. (UROT) -0.5 V
Focus Quad (FQUAD) -7.4 V
VG off
VV off
VVR off
VS2 off
VS3 off
TUNE DESCRIPTOR
eiposag
RESTORE
192.892
192.989
193.085
<>
><
<<
>>
^
v
C
V
LOCK
UNLK
TUNE:
Click


GC-LC Type: HP 6890 GC
GC ready
GC Descriptor
On Display: gc37
In GC : gc37
Current GC Temperature
Injector A
Transfer Line
Column
GC elapsed time
GC run time
Stabilize time
Column Oven
MID Set Up Parameters
MID File
Measure/lock ratio (X)
Set Damping relay (T)
Width first lock (A)
Electric jump time (E)
Magnetic jump time (D)
Offset (O)
Electric range (R)
Cycletime
Clear Masses
Main
MID Masses for Time Window 4
Lock Mass
Cali Mass
You are now ready to collect:
MPPSIRD
Double left click START in the analysis view.
SCAN
AUTOTUNE
TUNE
TUNE DESCRIPTOR
RESTORE
NOT ACQUIRING
START
METHOD LIST:
init(1)
SAVE
Click


GC-LC Type: HP 6890 GC
GC method is running
GC Descriptor
On Display: gc37
In GC
GC run time 23.0 Min
Injector A
But first, all GC temperatures n
correct and sta
Column: Constant Flow 0.1 ml/min
Inlet: Splitless Mode
Purge time 1.0
Purge flow 70.0
Saver time 3.0
Saver flow 15.0
Saver
Sequence No. 1 2 3 4 5 6
Time Min 1.0 16 2.4 13 6.0 1.0
Rate C/Min 5.0 25 3.0 10
Temp. C 60 60 140 200 240 300 300
Total Time 0 1.0 17 19 33 39 40
START GC
GC:
Simchr.icl sets the filament current to 0 until shortly before the first SIR group start time.
awaits the first SIR descriptor start time.
-11.0 V
0.00 mA
70.0 V
250 C
251 C
EI POS
U(a) 4769
Entr. Slit
Exit Slit
Sweep Mass
Virt. Mass
Link Mass
Sweep Width
Sweep Speed (SS) 1.0 /s
U(a) Offset (UOFS) 0.0 V
U(a)/U(esa) (URATIO) 2.025 %
Multiplier (EMULT) 1.60 kV
Dyn. Volt. (DYNODE) pos
Ref. Inlet (TREF) 150 C
Beam Rot. (UROT) -0.5 V
Focus Quad (FQUAD) -7.4 V
VG off VVR off
VV off VS2 off
VS3 off
TUNE DESCRIPTOR
eiposag
RESTORE
192.941 192.989 193.03
LOCK UNLK
TUNE:
MULTIPLE ION DETECTION
Lock Mass
Int 5
Mass 181.0
STATUS
MID File mid37
Windows 3
Measuring # 0
Mode
MID is not running
Elapsed time
ECORR 1.000219
EDACG 0.999820
EDACZ 1435
Cali. Mass
Int 11
Mass 193.0
Remarks:
Start MID
SAVE
Setup
MID:
NOT ACQUIRING
After the last SIR group data is recorded, the MID vi
Signal is recorded for the interval between the start and end times specified by the user.
Click

ICE is Easy A.H. Grange NERL, ESD, ECB

QUAN - group 1

File Defaults Display Parameters

Done reading defaults file

FILE | QuanF | write | 1_tbl | 2_tbls | Rep_1 | R

```
QUAN: andreas.q0                                   Entri

Data file(s) used
Fil1: demo1                              13-Dec-00
Samp: Vial 1 demo1                                 Start
Comm: Clark Co. effluent
Mode: EI +VE +LMR  ESCAN LR NRM
Oper:                                              Inlet

Disp: CHRO
Amount = (area * ref amnt) / (ref area * response fa
Response factors from quantitation file
```

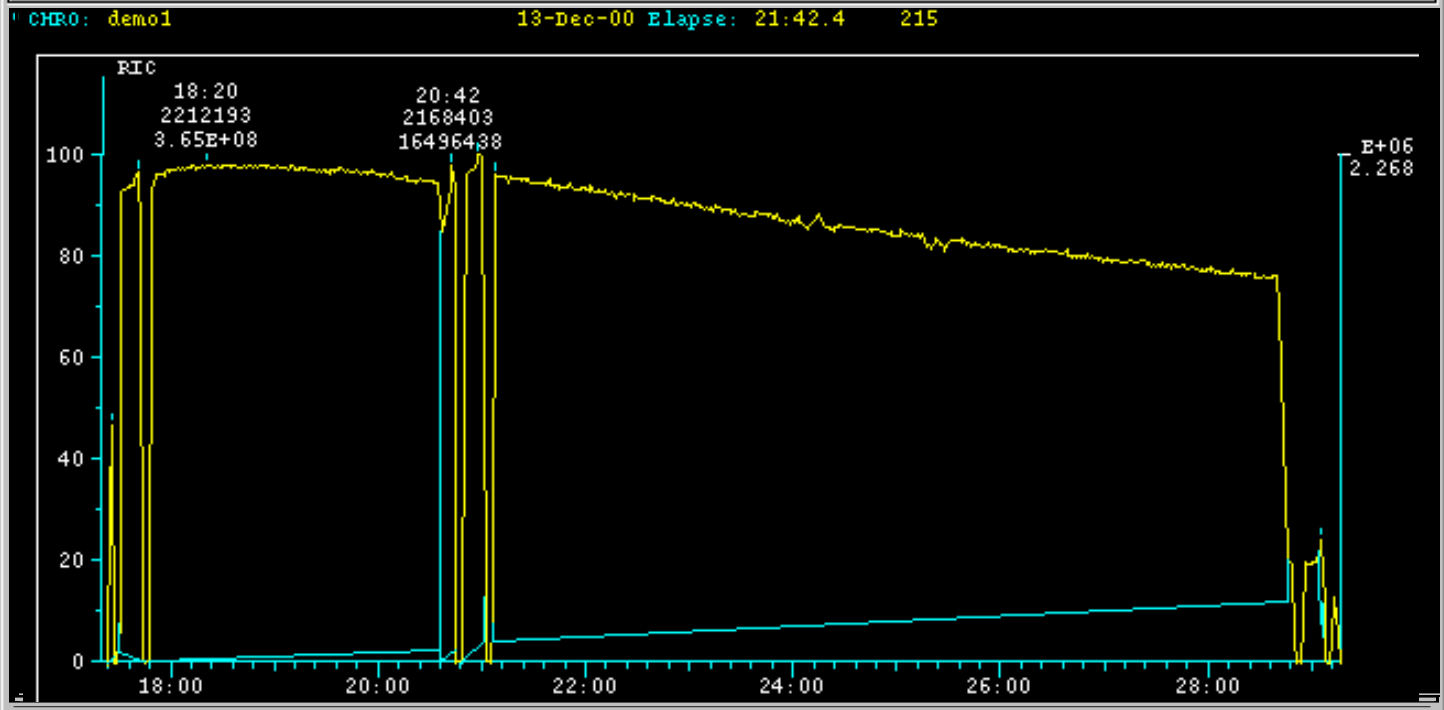
Quan Masses	Height	Area	Actual Time
192.9727	45270.	509144.	28:55
192.9791	62917.	722844.	28:55
192.9855	67157.	798735.	28:57
192.9920	57144.	672876.	29:00
192.9984	38237.	449699.	29:00
197.8686	2.	6.	29:07
197.9082	3.	7.	29:04
197.9479	4.	14.	29:01
197.9677	802.	7095.	28:54
197.9875	2593.	30654.	28:54
198.0073	539.	3886.	29:01
198.0271	9.	31.	28:58
198.0271	8289.	18875.	29:05
198.0469	66315.	155028.	29:05
198.0667	38507.	91424.	29:05
198.0865	35.	90.	28:54
198.0865	161.	561.	29:05
198.1261	70.	337.	28:58
198.1261	203.	600.	29:05
198.1459	172.	869.	29:05
198.1855	8.	20.	29:05
198.2450	3.	5.	28:59
198.2648	1.	2.	28:55
204.9718	27088.	310320.	28:54
204.9787	39473.	453776.	28:54
204.9857	53908.	617290.	28:54
204.9926	40418.	473261.	28:54
204.9996	26507.	332648.	28:54

CHRO - group 1

File Defaults Display Calculate Spectra Help

Done reading defaults file

All | s&rt | rt&a | 1000 mmu | 50 mmu | 2 mmu | d_all



DECterm

File Edit Commands Options Print Help

```
finnigan@icis5>
finnigan@icis5>
finnigan@icis5>
finnigan@icis6> cd ~/icl
finnigan@icis7> alias m csh mpp.icl
finnigan@icis8> m
finnigan@icis9>
```

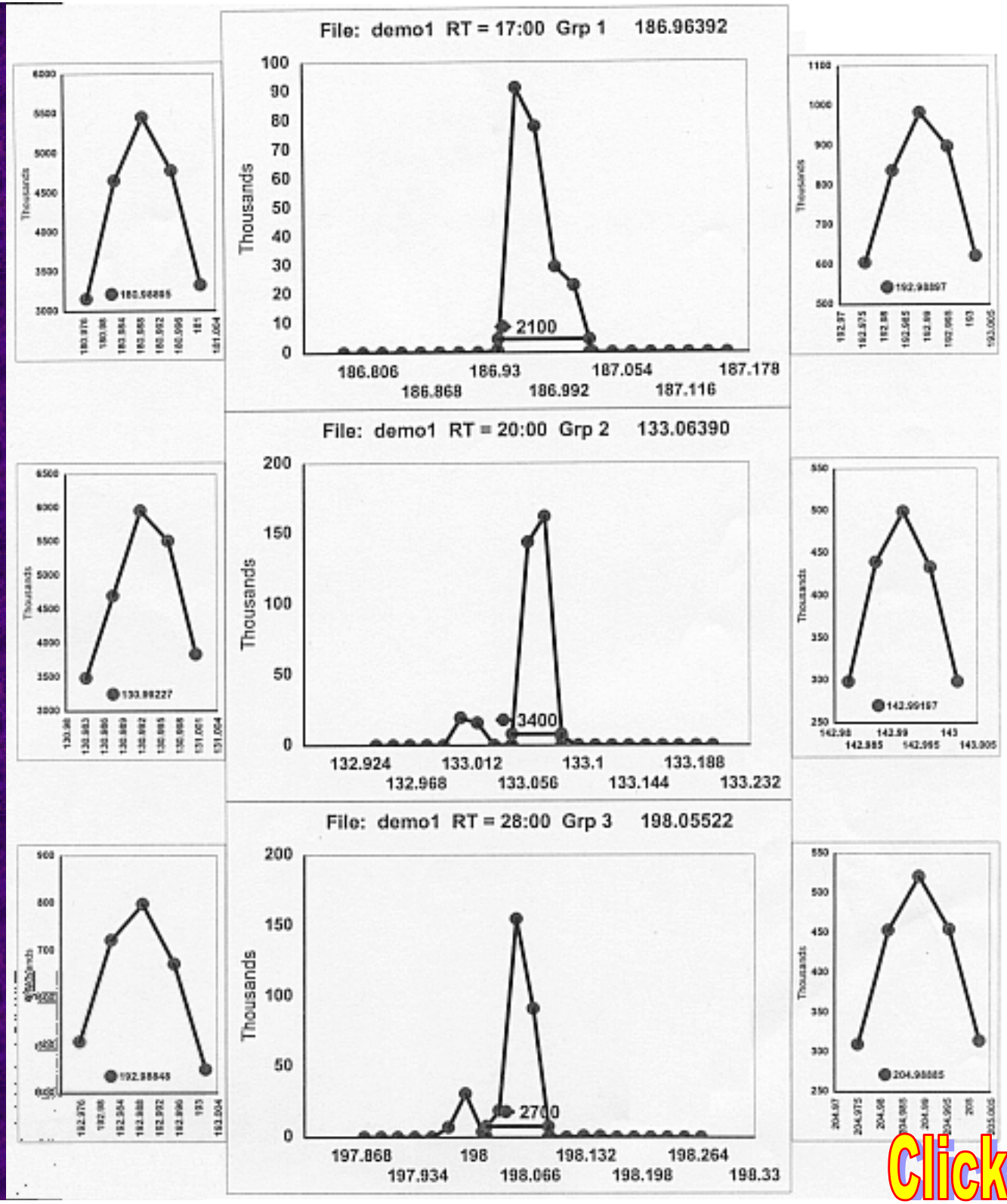
Enter cd ~/icl

Enter m

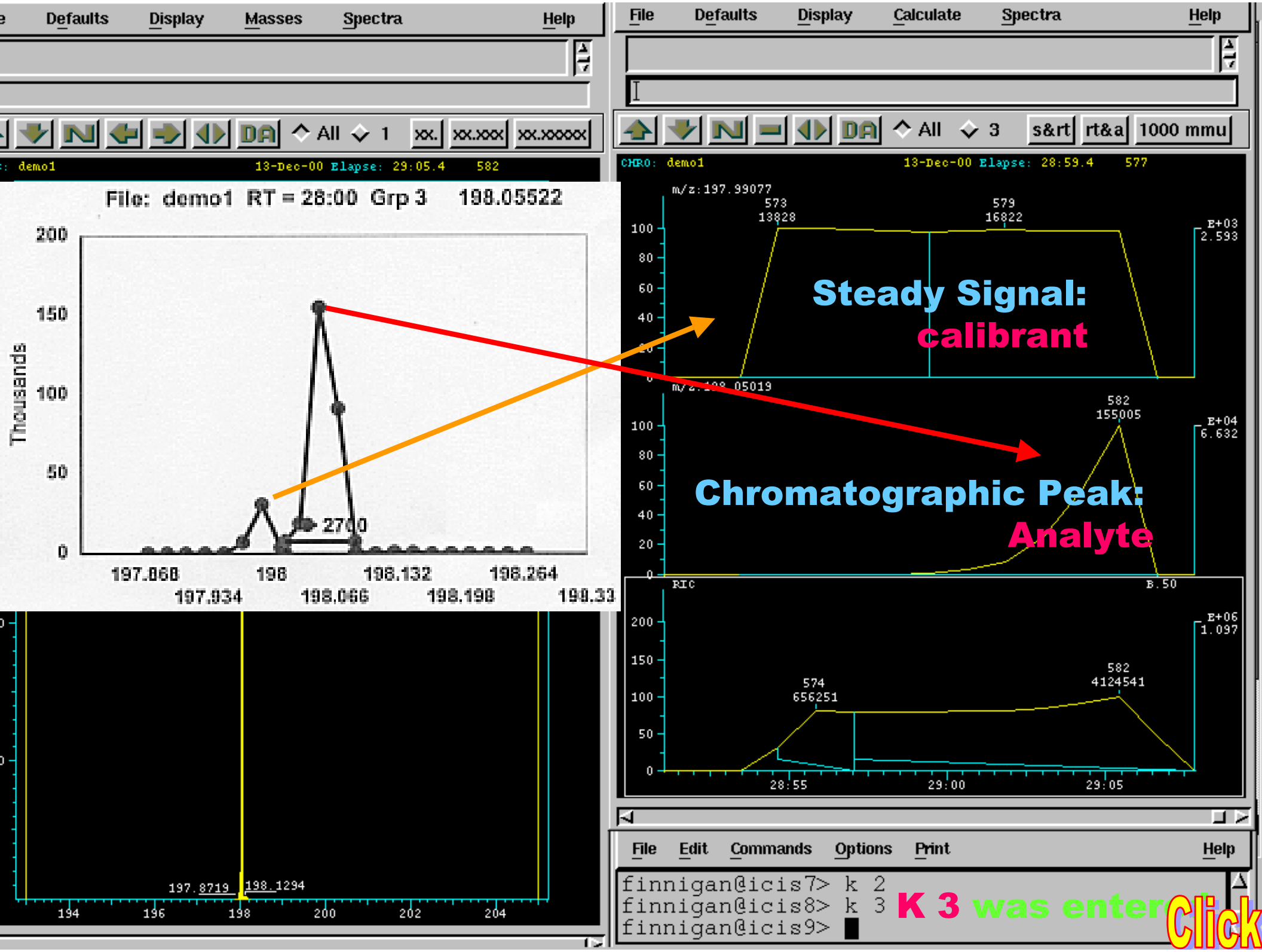
The cursor line reappears after *mpp.icl* is finished.

Click

The adjacent plots are printed for archiving.



Click


Defaults Display Masses Spectra Help
File Defaults Display Calculate Spectra Help
All 1 xx. xx.xxx xx.xxxxx
All 3 s&rt rt&a 1000 mmu
demo1 13-Dec-00 Elapse: 29:05.4 582
CHRO: demo1 13-Dec-00 Elapse: 28:59.4 577
File: demo1 RT = 28:00 Grp 3 198.05522
Thousands
197.868
197.934
198
198.066
198.132
198.198
198.264
198.33
m/z:197.99077
573
13828
579
16822
E+03
2.593
Steady Signal:
calibrant
582
155005
E+04
6.632
Chromatographic Peak:
Analyte
RIC
B.50
E+06
1.097
574
656251
582
4124541
28:55
29:00
29:05
197.8719
198.1294
194
196
198
200
202
204
File Edit Commands Options Print Help
finnigan@icis7> k 2
finnigan@icis8> k 3
finnigan@icis9>
K 3 was entered
Click

ICE is Easy A.H. Grange
NERL, ESD, ECB

NAM ^demo1

ENTER the Resolution, Center Masses & Times desired.

Allow at least 17 sec between each end time and the next start time.

ENTER <Cntl>G after last entry. ENTER <Cntl>B after data has been acquired.

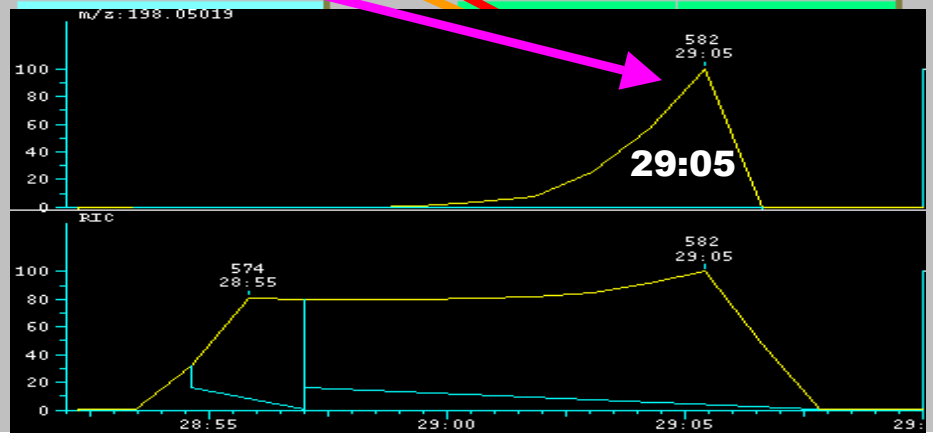
For all 3 SIR groups, the most abundant ion was an analyte ion. Had 10000 10000 FK ion had the greatest abundance, the user would estimate the mass of the ana enter it manually.

<Cntrl>Z enters 10,000 for both STEP and SLIT resolutions.

demo2

'K o

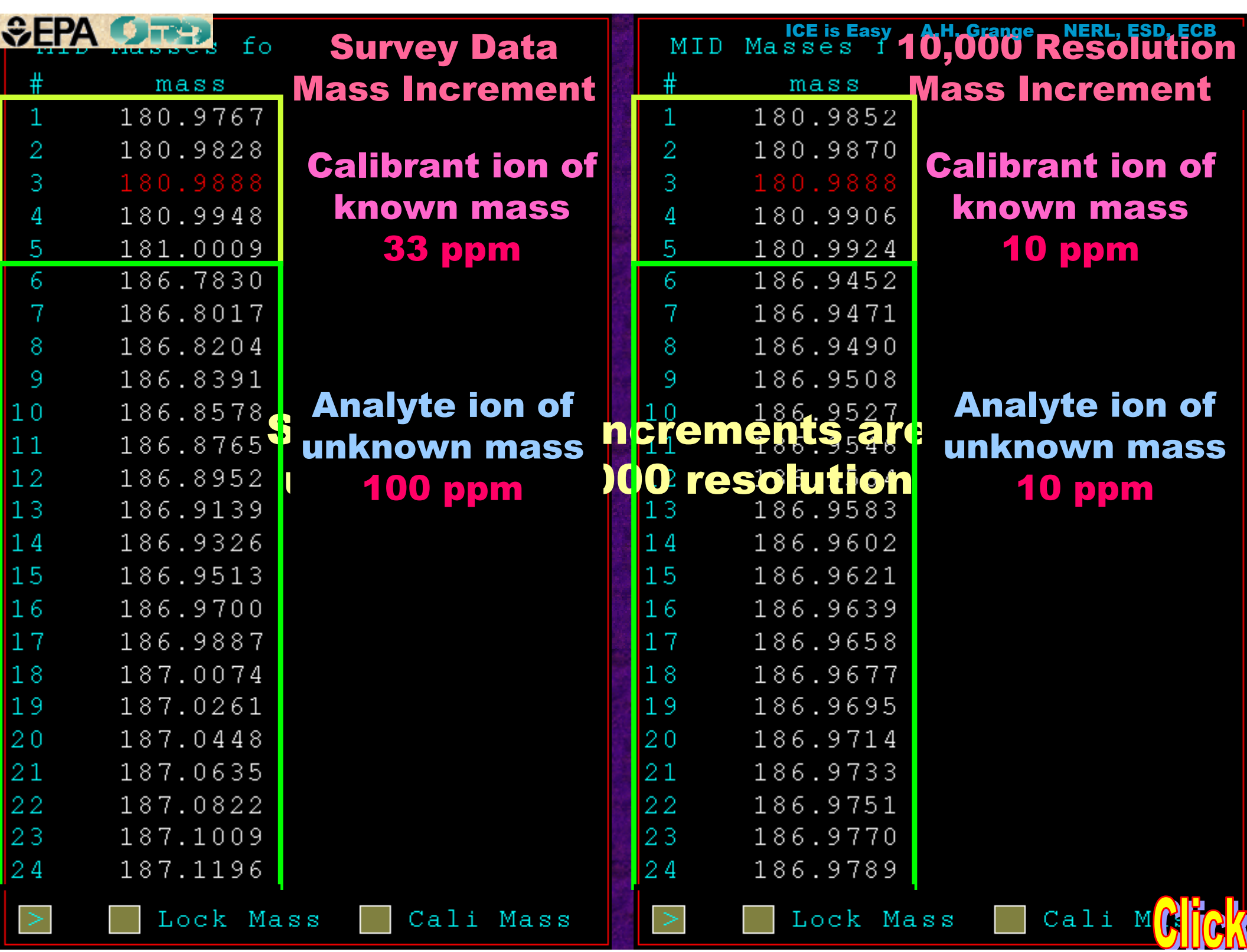
Center Mass	Start Time	End Time
186.07040	17:35	17:47
133.06390	20:52	21:04
198.05522	29:00	29:12



Enter <Cntrl>I to increment the Data Filename.

wide window 5 sec later, because the chromatographic peak maximum was missed.

Click


ICE is Easy
A.H. Grange
NERL, ESD, ECB
MID Masses fo
mass
1 180.9767
2 180.9828
3 180.9888
4 180.9948
5 181.0009
6 186.7830
7 186.8017
8 186.8204
9 186.8391
10 186.8578
11 186.8765
12 186.8952
13 186.9139
14 186.9326
15 186.9513
16 186.9700
17 186.9887
18 187.0074
19 187.0261
20 187.0448
21 187.0635
22 187.0822
23 187.1009
24 187.1196
Survey Data
Mass Increment
Calibrant ion of
known mass
33 ppm
Analyte ion of
unknown mass
100 ppm
> Lock Mass Cali Mass
MID Masses f
mass
1 180.9852
2 180.9870
3 180.9888
4 180.9906
5 180.9924
6 186.9452
7 186.9471
8 186.9490
9 186.9508
10 186.9527
11 186.9546
13 186.9583
14 186.9602
15 186.9621
16 186.9639
17 186.9658
18 186.9677
19 186.9695
20 186.9714
21 186.9733
22 186.9751
23 186.9770
24 186.9789
10,000 Resolution
Mass Increment
Calibrant ion of
known mass
10 ppm
Analyte ion of
unknown mass
10 ppm
> Lock Mass
Click

Review screens 7 through 17 to perform MPPSIRD at 10,000 resolution.

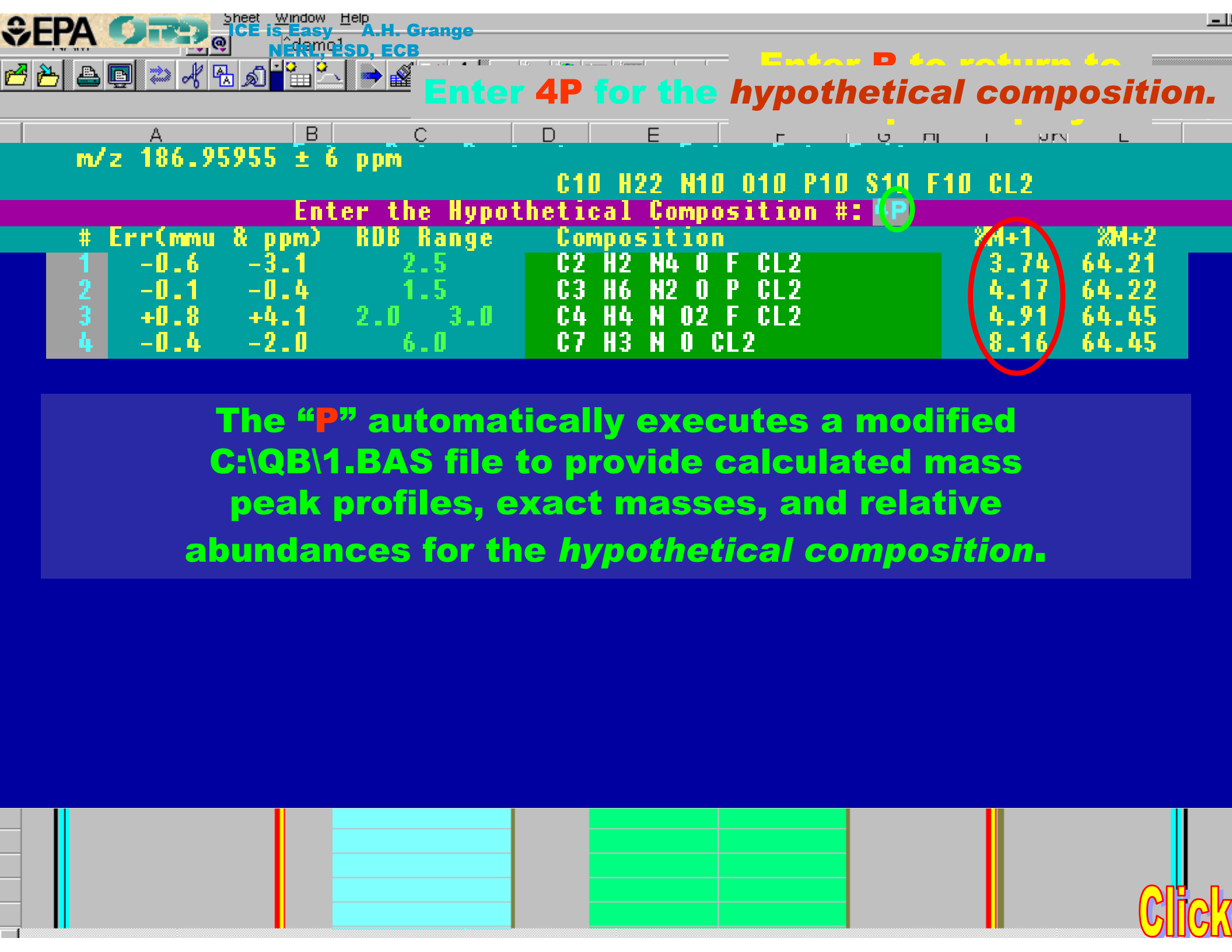
Midtune.icl contains two additional instructions:

fq
ur

These are subroutines that autotune the focus quadrupoles and the rotational quadrupoles.

These adjustments are only important at high mass resolution and are not performed by *Autotune*.

Click


ICE is Easy A.H. Grange
NERL, ESD, ECB
Enter 4P for the hypothetical composition.
m/z 186.95955 ± 6 ppm
C10 H22 N10 O10 P10 S10 F10 CL2
Enter the Hypothetical Composition #: 4P
Err(mmu & ppm) RDB Range Composition %M+1 %M+2
1 -0.6 -3.1 2.5 C2 H2 N4 O F CL2 3.74 64.21
2 -0.1 -0.4 1.5 C3 H6 N2 O P CL2 4.17 64.22
3 +0.8 +4.1 2.0 3.0 C4 H4 N O2 F CL2 4.91 64.45
4 -0.4 -2.0 6.0 C7 H3 N O CL2 8.16 64.45
The "P" automatically executes a modified C:\QB\1.BAS file to provide calculated mass peak profiles, exact masses, and relative abundances for the hypothetical composition.
Click

ENTER the Resolution, Center Masses & Times desired.

Allow at least 17 sec between each end time and the next start time.

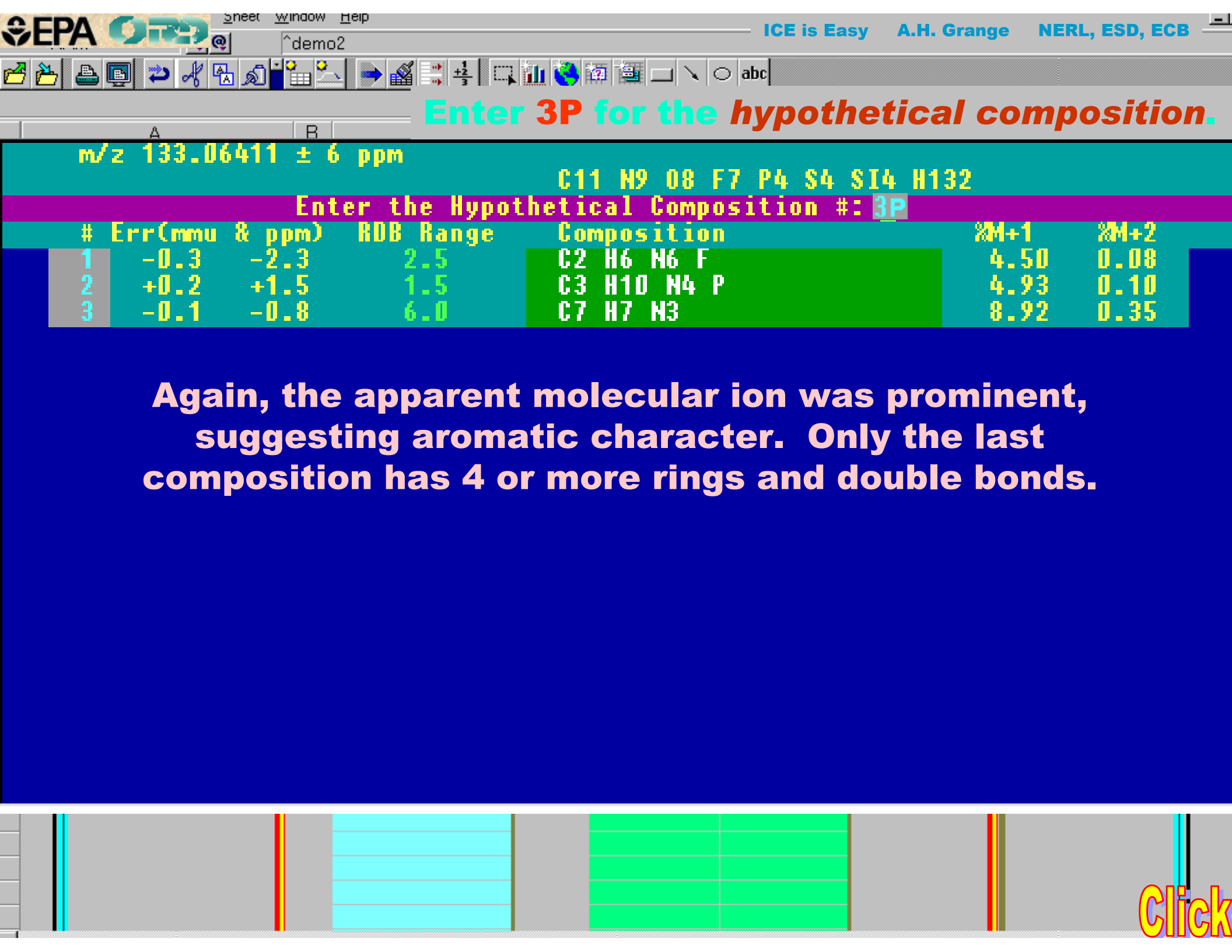
ENTER <Cntl>G after last entry. **ENTER <Cntl>B after data has been acquired.**

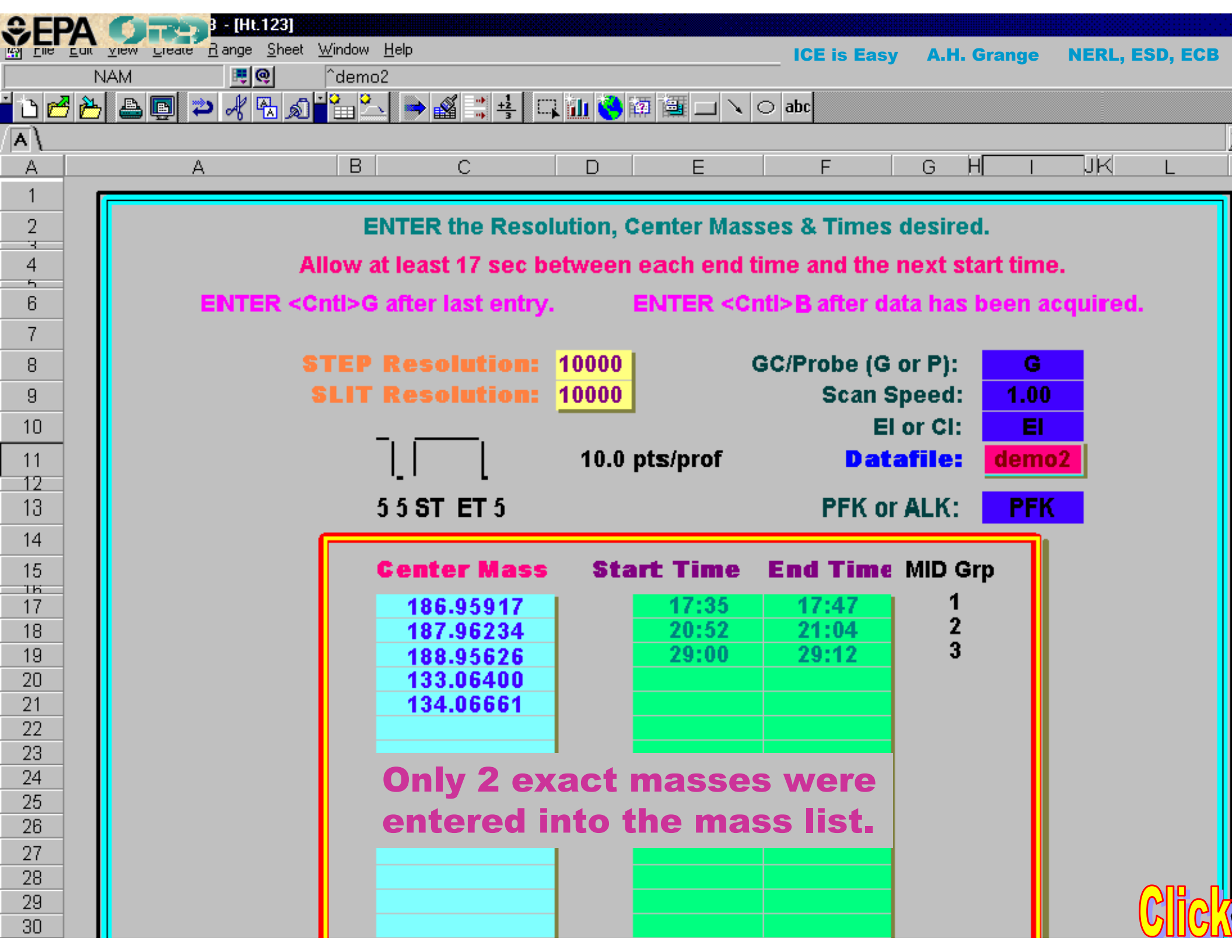
STEP Resolution:	10000	**GC/Probe (G or P):**	G
SLIT Resolution:	10000	**Scan Speed:**	1.00
		EI or CI:	EI
10.0 pts/prof		**Datafile:**	demo2
5 5 ST ET 5		**PFK or ALK:**	PFK

Center Mass	Start Time	End Time	MID Grp
186.95917	17:35	17:47	1
187.96234	20:52	21:04	2
188.95626	29:00	29:12	3

The 3 exact masses were entered into the mass list. Enter <Cntrl>Y, if an error was made (e.g. the wrong SIR group was considered) to remove the last masses entered.

Click


Sheet Window Help
ICE is Easy A.H. Grange NERL, ESD, ECB
^demo2
Enter 3P for the hypothetical composition.
m/z 133.06411 ± 6 ppm
C11 N9 O8 F7 P4 S4 SI4 H132
Enter the Hypothetical Composition #: 3P
Err(mmu & ppm) RDB Range Composition %M+1 %M+2
1 -0.3 -2.3 2.5 C2 H6 N6 F 4.50 0.08
2 +0.2 +1.5 1.5 C3 H10 N4 P 4.93 0.10
3 -0.1 -0.8 6.0 C7 H7 N3 8.92 0.35
Again, the apparent molecular ion was prominent, suggesting aromatic character. Only the last composition has 4 or more rings and double bonds.
Click


EPA
- [Ht.123]
File Edit View Create Range Sheet Window Help
ICE is Easy A.H. Grange NERL, ESD, ECB
NAM
^demo2
ENTER the Resolution, Center Masses & Times desired.
Allow at least 17 sec between each end time and the next start time.
ENTER <Cntl>G after last entry.
ENTER <Cntl>B after data has been acquired.
STEP Resolution: 10000
SLIT Resolution: 10000
GC/Probe (G or P): G
Scan Speed: 1.00
EI or CI: EI
Datafile: demo2
PFK or ALK: PFK
10.0 pts/prof
5 5 ST ET 5
Center Mass
Start Time
End Time
MID Grp
186.95917
187.96234
188.95626
133.06400
134.06661
17:35
17:47
20:52
21:04
29:00
29:12
1
2
3
Only 2 exact masses were entered into the mass list.
Click

Sheet Window Help

^demo2 ICE is Easy A.H. Grange NERL, ESD, ECB

Enter 16P for the *hypothetical composition*.

m/z 198.05576 ± 6 ppm

C16 N14 O12 F10 P6 S6 SI7 H196

Enter the Hypothetical Composition #: 16 P

#	Err(mmu	& ppm)	RDB	Range	Composition	%M+1	%M+2
1	+0.8	+4.3	-1.0	0.0	C5 H18 O2 S SI2	16.77	12.67
2	+0.2	+1.0		0.0	C5 H14 O6 SI	11.01	5.01
3	-0.4	-2.0		1.0	C5 H13 N2 F2 P SI	11.50	3.86
4	+0.4	+2.2		5.5	C5 H8 N7 S	8.99	4.80
5	+0.1	+0.6		0.0	C6 H17 F P2 SI	11.93	3.91
6	+1.1	+5.4	-1.0	0.0	C6 H18 O S2 SI	13.56	13.17
7	-1.2	-5.8	0.0	1.0	C6 H15 O2 F S SI	12.77	8.84
8	+0.4	+2.2	0.0	1.0	C6 H14 O5 S	7.80	5.70
9	+0.4	+2.2		1.5	C6 H11 N O F3 SI	12.25	4.15
10	-0.9	-4.7	0.0	1.0	C7 H15 O F S2	9.56	9.47
11	+0.7	+3.4		1.5	C7 H11 N F3 S	9.04	4.79
12	-0.5	-2.3	6.0	7.0	C7 H7 N4 O2 F	9.36	0.79
13	+0.1	+0.3	5.0	6.0	C8 H11 N2 O2 P	9.79	0.83
14	-0.7	-3.5		5.5	C9 H10 N F2 SI	15.50	4.38
15	+0.9	+4.5	5.5	6.5	C9 H9 N O3 F	10.53	1.10
16	-0.3	-1.3	9.5	10.5	C12 H8 N O2	13.79	1.28

Of these, the last composition has the fewest heteroatoms and is chosen as the *hypothetical composition*. The composition with the fewest heteroatoms is correct in the majority of cases.

Click

ENTER the Resolution, Center Masses & Times desired.

Allow at least 17 sec between each end time and the next start time.

ENTER <Cntl>G after last entry. ENTER <Cntl>B after data has been acquired.

STEP Resolution:	10000
SLIT Resolution:	10000

10.0 pts/prof

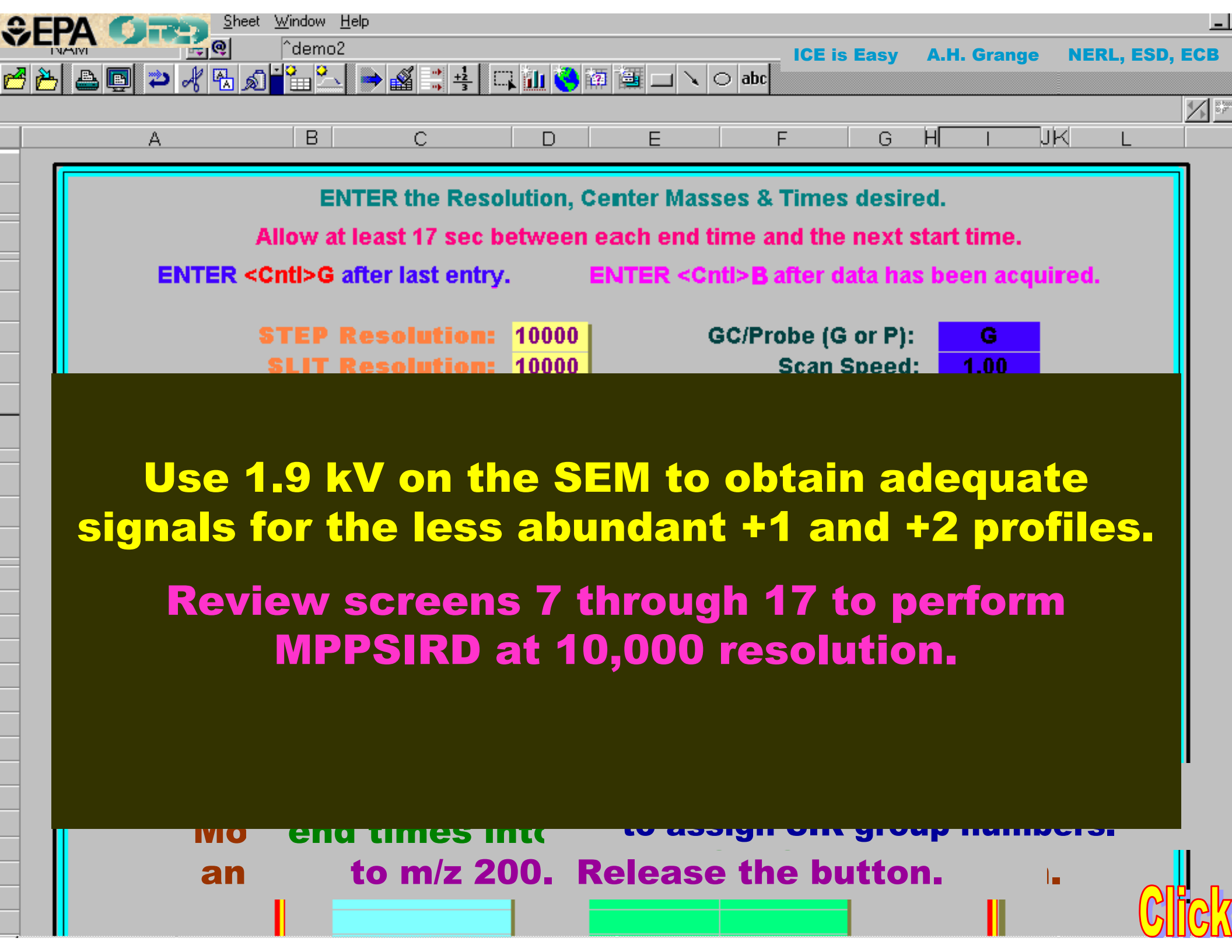
5 5 ST ET 5

GC/Probe (G or P):	G
Scan Speed:	1.00
EI or CI:	EI
Datafile:	demo2
PFK or ALK:	PFK

Center Mass	Start Time	End Time	MID Grp
186.96392	17:35	17:46	1
133.0639	20:50	21.02	2
198.05522	29:01	29:13	3
133.064			3
134.06661			3
198.0555			3
199.05877			3
200.06129			3

The 3 exact masses for the third analyte were added to the mass list.

Click


Sheet Window Help
^demo2
ICE is Easy A.H. Grange NERL, ESD, ECB
ENTER the Resolution, Center Masses & Times desired.
Allow at least 17 sec between each end time and the next start time.
ENTER <Cntl>G after last entry.
ENTER <Cntl>B after data has been acquired.
STEP Resolution: 10000
SLIT Resolution: 10000
GC/Probe (G or P): G
Scan Speed: 1.00
Use 1.9 kV on the SEM to obtain adequate signals for the less abundant +1 and +2 profiles.
Review screens 7 through 17 to perform MPPSIRD at 10,000 resolution.
to m/z 200. Release the button.
Click

ICE is Easy A.H. Grange
NERL, ESD, ECB

Lock Mass

The first tw… *mpp1.lcl* as p…

Multiple analy…

m/z 133

+1

Cal. Mass

…ors written by …*e.icl* are shown.

…ll be monitored.

MID Masses for Time … 1

#	mass	F	int	…me(ms)
1	180.9852		1	20.48
2	180.9870		1	20.48
3	180.9888			
4	180.9906			
5	180.9924			
6	186.9536			
7	186.9554			
8	186.9573			
9	186.9592			
10	186.9610		1	20.48
11	186.9629		1	20.48
12	186.9648		1	20.48
13	187.9567		1	20.48
14	187.9586		1	20.48
15	187.9605		1	20.48
16	187.9623		1	20.48
17	187.9642		1	20.48
18	187.9661		1	20.48
19	187.9680		1	20.48
20	188.9506		1	20.48
21	188.9525		1	20.48
22	188.9544		1	20.48
23	188.9563		1	20.48
24	188.9581		1	20.48
25	188.9600		1	20.48
26	188.9619		1	20.48
27	192.9850		1	20.48
28	192.9869		1	20.48
29	192.9888	c	1	20.48
30	192.9908		1	20.48
31	192.9927		1	20.48

< Lock Mass … Mass

MID Masses for Time … 2

#	mass	F	int	…me(ms)
1	130.9894		1	21.84
2	130.9907		1	21.84
10	133.0633			
11	133.0647			
12	133.0660			
13	133.0673			
14	133.0687			
15	133.0700		1	21.84
16	134.0606			
17	134.0619			
18	134.0633			
19	134.0646			
20	134.0659			
21	134.0673			
22	134.0686			
23	134.0700			
24	134.0713			
25	134.0726		1	21.84
26	142.9891		1	21.84
27	142.9906		1	21.84
28	142.9920	c	1	21.84
29	142.9934		1	21.84
30	142.9948		1	21.84
31				

< Lock Mass … Click

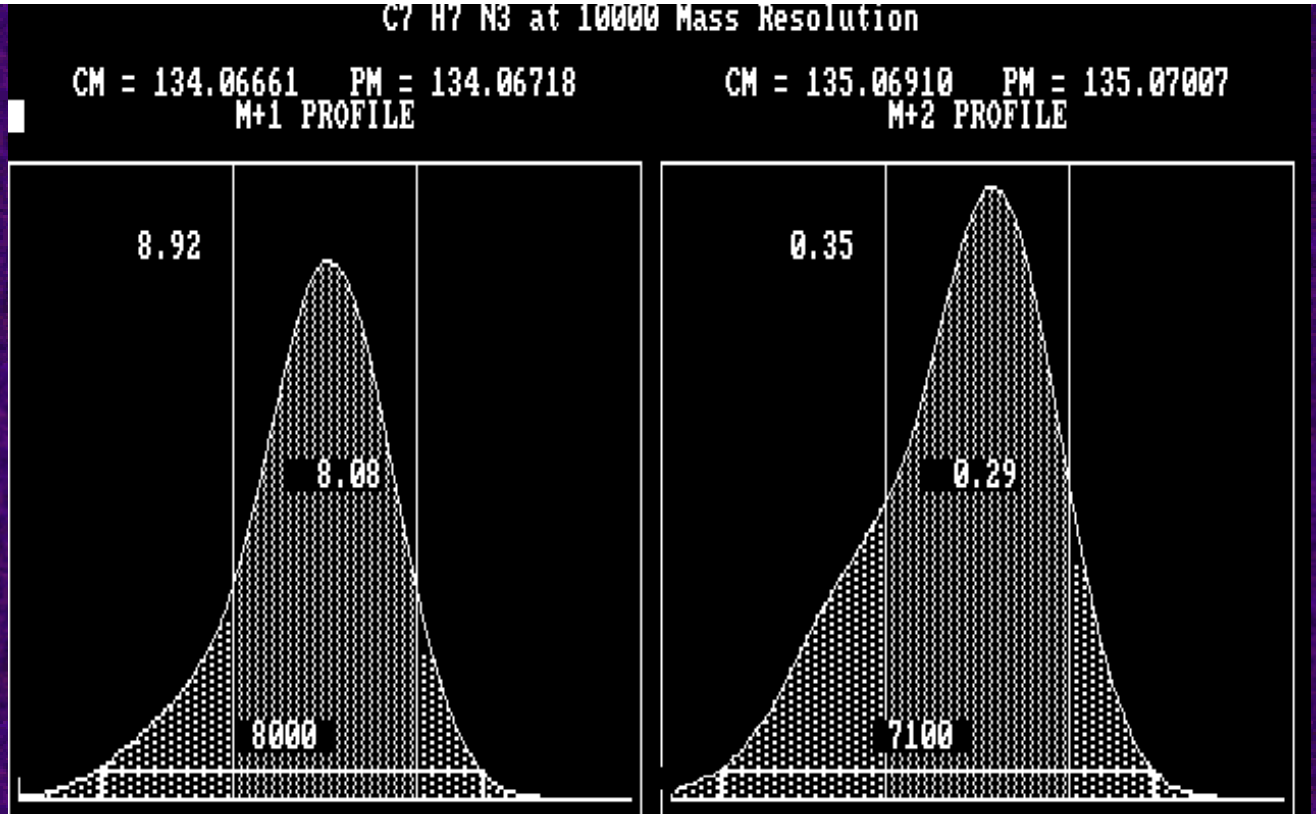
#	RDB Range	Composition	M	M+1	M+2	%M+1 (%M+1 Range)	%M+2 (%M+2 Range)
1	-2.0 0.0	H4 N O3 F3 S2	.95847	.95780 X	.95441 X	0.62(0.15-1.22) X	8.27(6.39-10.09) X
2	-0.5 0.5	N2 O2 F5 S	.96006	.95854 X	.95611	0.65(0.17-1.33) X	4.80(3.76-5.96) X
3	2.5 3.5	H2 N4 O3 F P2	.95862	.95591 X	.96279 X	0.16(0.01-0.40) X	0.03(0.00-0.13) X
4	1.5 4.5	H3 N4 O4 S2	.95957	.95812 X	.95561	1.03(0.24-2.14) X	9.19(7.39-11.10) X
5	-0.5 0.5	C H O3 F5 P	.95835	.96181	.96260 X	1.26(1.05-1.47) X	0.02(0.00-0.14) X
6	2.0 3.0	C H N O10	.96005	.96283	.96429 X	1.79(1.37-2.26) X	0.01(0.00-0.18) X
7	1.5 2.5	C H6 N2 O3 P3	.95913	.96082 X	.96333 X	1.51(1.04-2.04) X	0.01(0.00-0.09) X
8	3.0 5.0	C N3 O4 F2 P	.95945	.95996 X	.96362 X	1.54(0.91-2.28) X	0.01(0.00-0.11) X
9	1.5	C H4 N4 F S3	.95821	.95778 X	.95403 X	1.44(0.46-2.68) X	10.77(7.41-13.89) X
10	2.5 3.5	C H2 N4 O2 F P CL	.95879	.95867 X	.95590	1.23(0.66-1.92) X	32.36(25.37-39.99) X
11	2.0	C H4 N5 P CL2	.95814	.95727 X	.95519	0.88(0.39-1.50) X	63.99(51.37-77.73)
12	2.0 4.0	C2 H4 N O4 F P2	.95996	.96299	.96423 X	2.70(2.18-3.26) X	0.00(0.00-7.00) X
13	2.0 4.0	C2 H2 N O6 F S	.95869	.96074 X	.95537	2.93(2.07-3.81) X	4.89(4.09-5.81) X
14	0.5	C2 H8 N2 P S3	.95872	.95955 X	.95455 X	3.21(1.76-4.82) X	11.71(8.35-14.92) X

Again, a blank row between the last and preceding compositions indicate that *only* the last composition was consistent with all 5 measured values. All other possible compositions based on the Exact Mass of the m/z 187 ion were rejected by comparing the measured and calculated values of Exact Masses and Relative Abundances for the +1 and +2 partial profiles. At least 1 X is seen in each other composition's row.

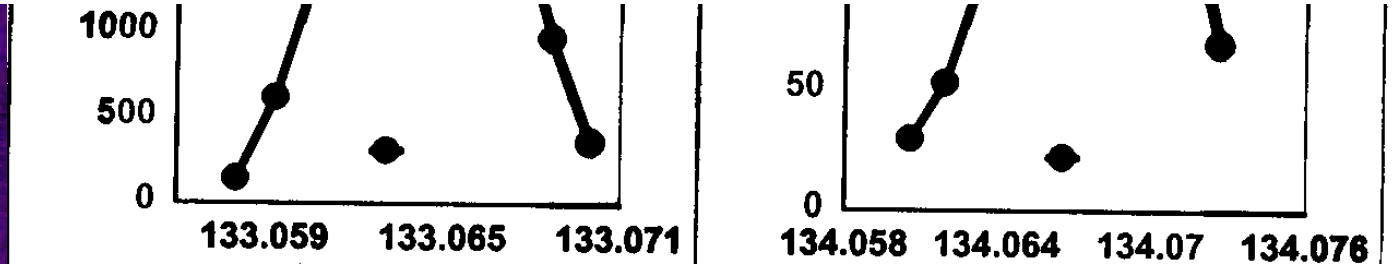
31	5.0	C6 H5 N S3	.95841	.96064 X	.95435 X	7.92(5.90-9.94)	11.48(8.27-14.51) X
32	6.0 7.0	C6 H3 N O2 P CL	.95899	.96214	.95613	6.99(5.98-8.02)	32.27(25.36-39.79) X
33	6.5					)	4.10(3.21-4.97) X
34	6.5					)	31.91(25.08-39.30) X
36	10.5 1					89) X	0.01(0.00-0.12) X
37	10.5					50) X	32.74(25.20-41.04) X
35	6.0	C7 H3 N O CL2	.95917	.96234	.95626	8.05(6.90-9.24)	64.01(50.11-79.05)
Experimental Values:			.95915	.96232	.95616	7.39	64.3

The *hypothetical composition* was correct: $C_7H_3NOCl_2$

Click



With a step resolution of 10,000, the 5% levels were not monitored for these broadened profiles. A step resolution of 6700 would usually ensure observation of 5% of profile maximum levels with a slit resolution of 10,000. Because both +1 and +2 partial profiles were monitored for two analytes, 10,000 resolution was preferred.



Click

m/z = 198.05538 ± 6 ppm C16 N14 O12 F10 P6 S6 SI7 H196 Resolution: 10000

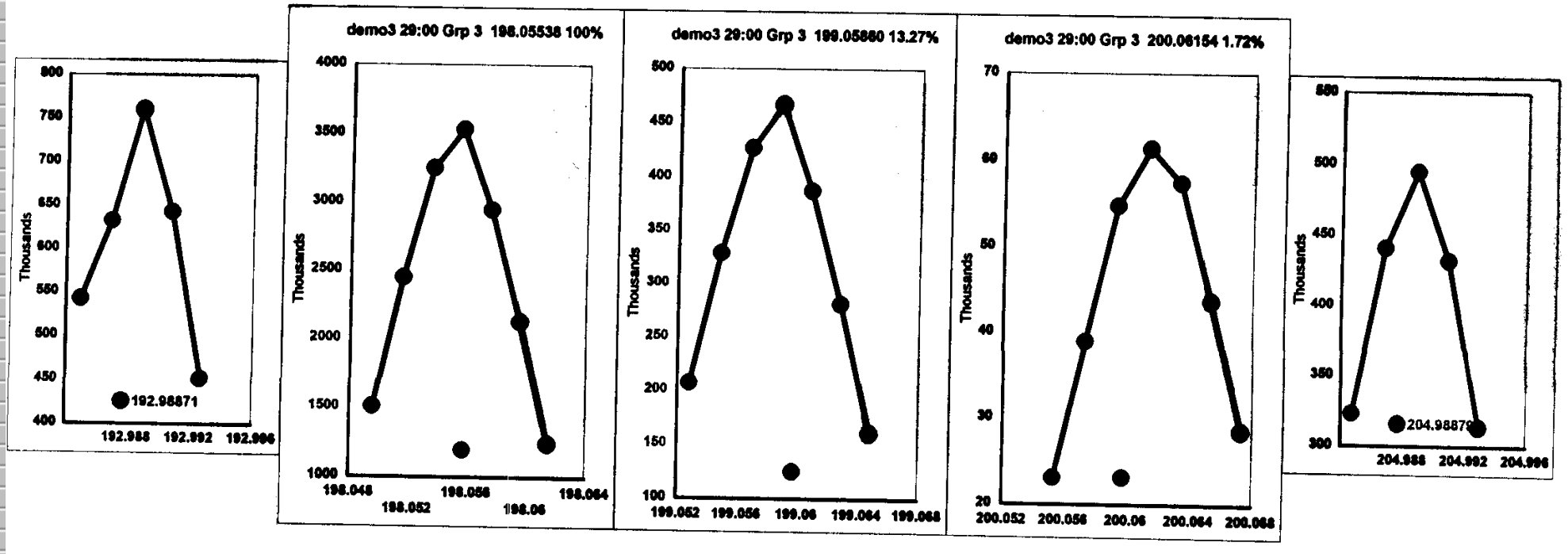
#	RDB	Range	Composition	M	M+1		M+2		%M+1 (%M+1 Range)		%M+2 (%M+2 Range)	
1	1.0		H11 N8 O P SI	.05627	.05504	X	.05337	X	3.92(1.51-7.18)	X	0.11(0.00-0.40)	X
2	2.0		H7 N10 F S	.05599	.05355	X	.05177	X	0.99(0.13-2.40)	X	0.01(0.00-0.16)	X
3	1.0		C H11 N8 P S	.05650	.05518	X	.05233	X	3.03(1.36-5.26)	X	0.02(0.00-0.24)	X
4	2.0		C H8 N8 O F P	.05427	.05282	X	.05762	X	0.98(0.38-1.78)	X	0.10(0.03-0.18)	X
5	-0.5	0.5	C2 H16 N3 O2 SI3	.05503	.05495	X	.05237	X	8.77(4.09-14.27)		0.13(0.00-0.56)	X
6	1.0		C2 H12 N6 O P2	.05478	.05527	X	.05833	X	2.46(1.46-3.63)	X	0.16(0.08-0.25)	X
7	2.5	3.5	C2 H6 N7 O2 F2	.05510	.05521	X	.05888	X	2.56(1.42-3.94)	X	0.33(0.17-0.50)	X
8	6.0		C2 H6 N10 SI	.05462	.05409	X	.05164	X	3.75(1.60-6.49)	X	0.01(0.00-0.09)	X
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
22												
23												
24												
25												
26												
27												
28	2.5								.43)	X	0.46(0.36-0.56)	X
29	6.0	7.0							.50)	X	0.68(0.47-0.91)	X
30	5.0	6.0							.10)	X	0.80(0.6	X
31	5.5								16.65)		0.32(0.0	
32	9.5	10.5	C12 H8 N O2	.05550	.05877		.06130		13.73(11.79-15.68)		1.25(1.02-1.49)	
Experimental Values:				.05538	.05860		.06125		13.27		1.26	

Alternatively, one could repeat data acquisition over a narrower time window to discriminate against the interfering ion.

The *hypothetical composition* was correct: $C_{12}H_8NO_2^+$

Click

Lock Mass	m/z 198	+1	+2	Cal. Mass



Mass			Mass			Mass			Mass		
192.98496	543265		198.04956	1510919		199.05280	207608		200.05529	23122		204.98472	323446	
192.98689	633411		198.05154	2453982		199.05479	329295		200.05729	39002		204.98677	441194	
192.98882	760773		198.05352	3256842		199.05678	427492		200.05929	54867		204.98882	495096	
192.99075	643767		198.05550	3535016		199.05877	467209		200.06129	61469		204.99087	432224	
192.99268	452116		198.05748	2952665		199.06076	387838		200.06329	57528		204.99292	313807	
			198.05946	2132532		199.06275	282175		200.06529	43771				
192.98882	606444.5	192.98871	198.06144	1244582		199.06474	161460		200.06729	28612		204.98882	404451.5	204.98879
					198.05538			199.05860			200.06154			
					100%			13.27%			1.72%			

Click

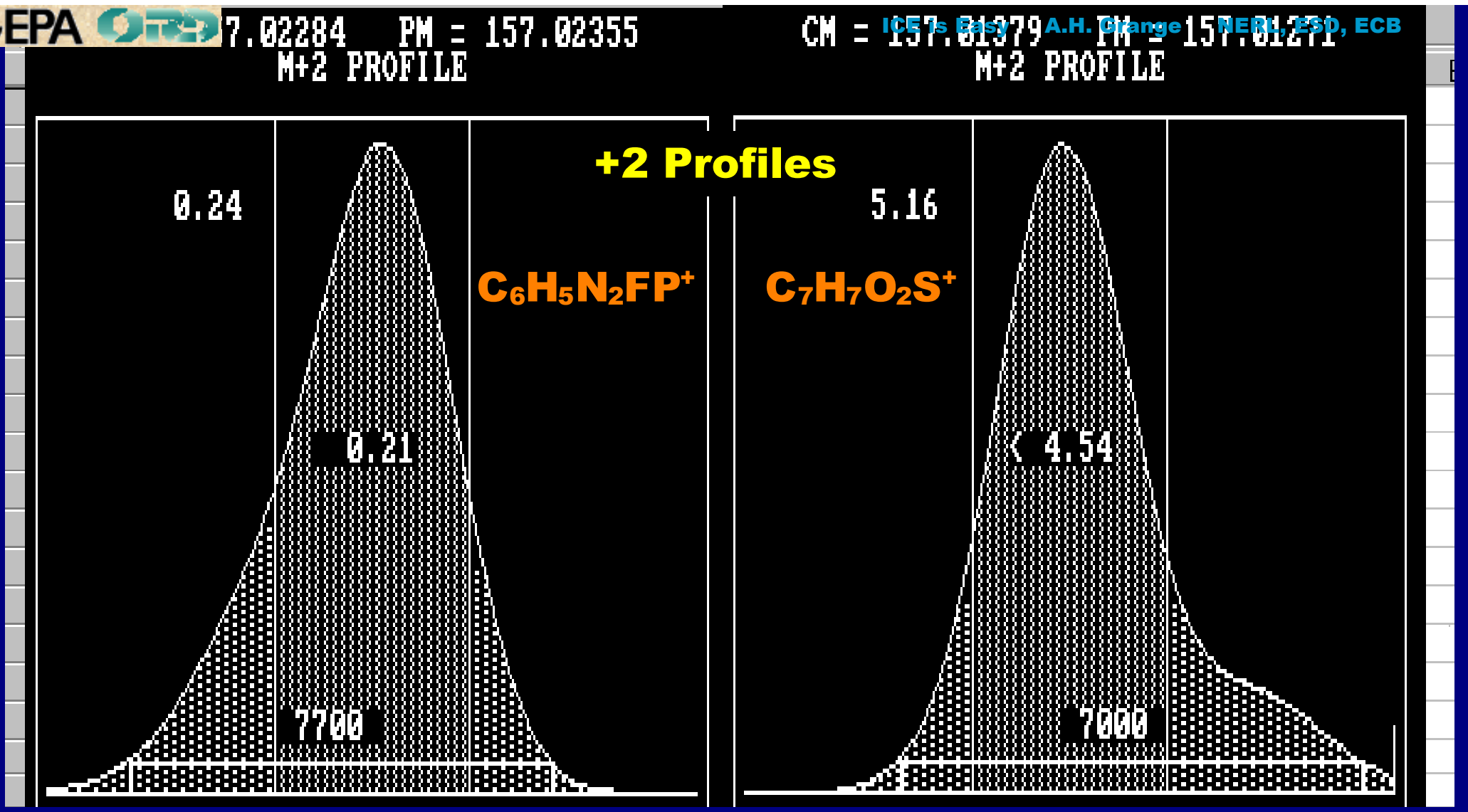
C:\WINNT\System32\CMD.exe

c:\IVA\Ht.123

	EI	EJ	EK	EL	EM	EN	EO	EP	EQ
3	m/z = 152.99798 ± 6 ppm				C12 N10 O9 F8 P4 S4 CL4 H151				Resolution:
4									
5	# RDB Range	Composition		M	M+2			%M+2	(%M+2 Range)
6									
7	1 2.5 3.5	C H3 N4 O2 F P		.99777	.00168	X		0.43	(0.36-0.50) X
8	2 2.0	C H5 N5 P CL		.99711	.99416	X		32.01	(25.70-38.89)
9	3 1.5 2.5	C2 H7 N2 O2 P2		.99828	.00245	X		0.44	(0.36-0.51) X
10	4 3.0 4.0	C2 H N3 O3 F2		.99860	.00269	X		0.65	(0.54-0.76) X
11	5 2.5	C2 H3 N4 O F CL		.99794	.99504			32.24	(25.89-39.15)
12	6 1.5	C3 H7 N2 O P CL		.99845	.99556			32.25	(25.90-39.17)
13	7 6.5	C3 [illegible]							(4.00-5.21) X
14	8 1.5	C4 [illegible]							(51.44-77.84)
15	9 2.5	C5 [illegible]							(4.00-5.21) X
16	10 7.0 8.0	C5 [illegible]							(0.49-0.70) X
17	11 6.0 7.0	C6 H4 N O2 P		.99797	.00286	X		0.62	(0.52-0.73) X
18	12 6.5	C7 H2 O3 F		.99880	.00383	X		0.87	(0.73-1.02) X
19	14 10.5	C10 H O2		.99765	.00336	X		0.97	(0.81-1.13) X
20									
21	13 6.0	C7 H4 N O CL		.99814	.99532			32.48	(26.09-39.43)
22									
23	Experimental Values:			.99798	.99505			31.14	
24									

A single composition is now consistent with the 3 measured values.

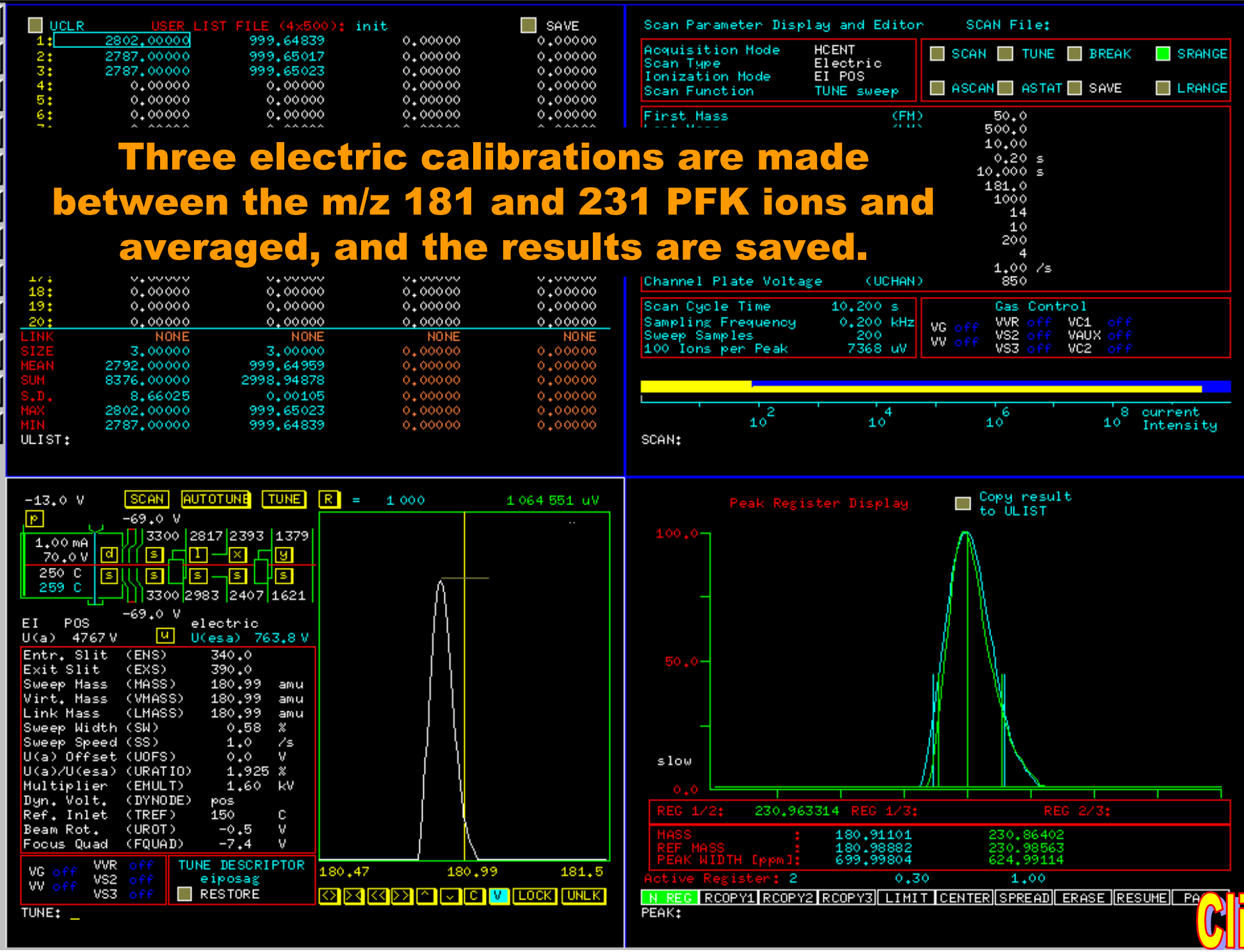
Click

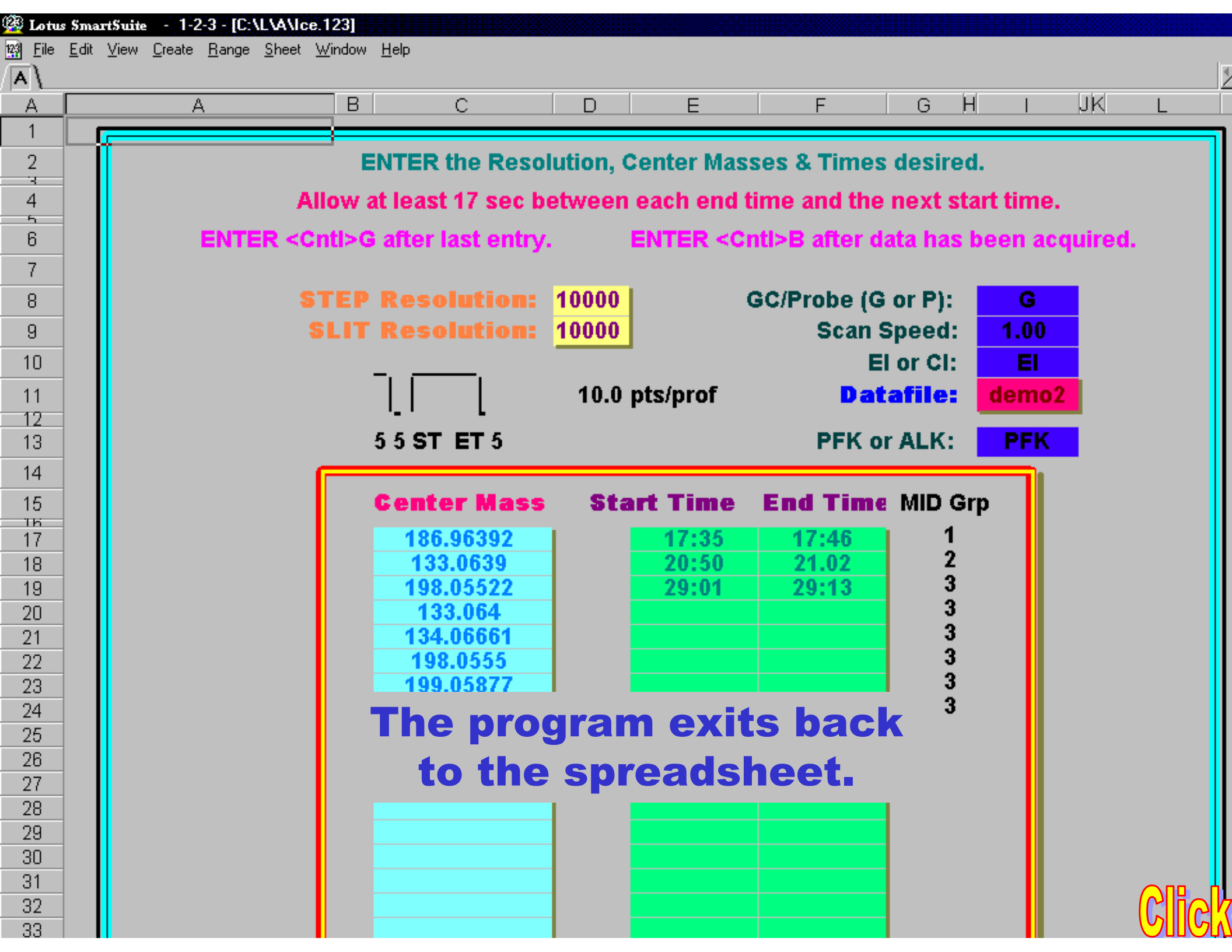


However, for the second composition, a good estimate of the Exact Mass would still be provided. Monitoring the +2 profile would distinguish between these compositions.

Click

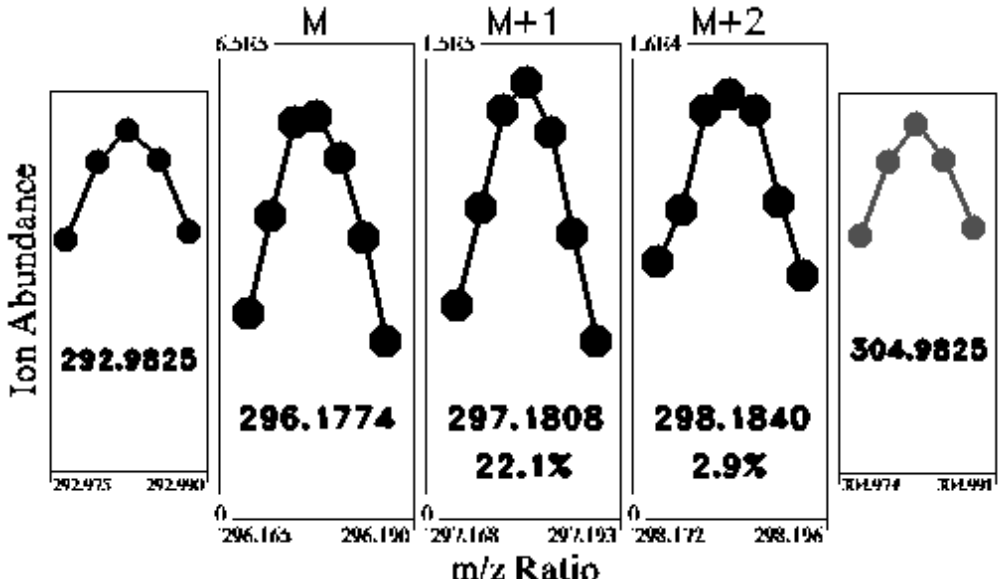
Three electric calibrations are made between the m/z 181 and 231 PFK ions and averaged, and the results are saved.

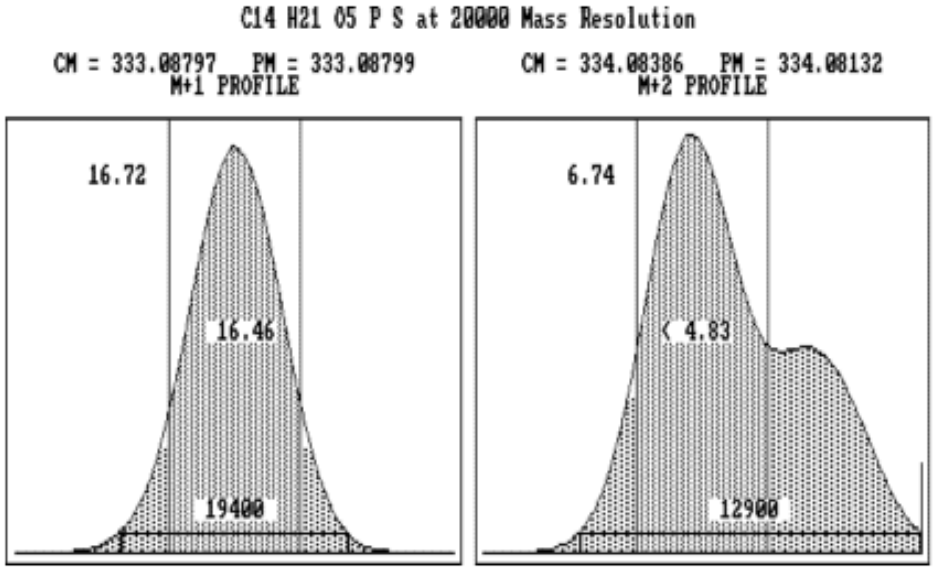



Lotus SmartSuite - 1-2-3 - [C:\L\A\Ice.123]
File Edit View Create Range Sheet Window Help
ENTER the Resolution, Center Masses & Times desired.
Allow at least 17 sec between each end time and the next start time.
ENTER <Cntl>G after last entry.
ENTER <Cntl>B after data has been acquired.
STEP Resolution: 10000
SLIT Resolution: 10000
10.0 pts/prof
5 5 ST ET 5
GC/Probe (G or P): G
Scan Speed: 1.00
EI or CI: EI
Datafile: demo2
PFK or ALK: PFK
Center Mass
Start Time
End Time
MID Grp
186.96392
133.0639
198.05522
133.064
134.06661
198.0555
199.05877
17:35
17:46
20:50
21.02
29:01
29:13
1
2
3
3
3
3
3
3
The program exits back to the spreadsheet.
Click

MPPSIRDware Manual ICE Profile Generation Model Manual

These manuals discuss all of the MPPSIRD and the Profile Generation Model code.





However, the MPPSIRDware manual describes Lotus 123 v2.2 and WordPerfect 5.1 code no longer used. The manual has not been updated to describe the new Lotus 123 v9.x code currently used. The PGM manual in Quick Basic fails to describe only a few features that have been added to permit its use directly from the spreadsheet.

Click

Articles about ICE

Grange, A.H.; Osemwengie, L.; Brilis, G.; Sovocool, G.W. "Ion Composition Elucidation (ICE): An Investigative Tool for Characterization and Identification of Compounds of Regulatory Importance" *International J. of Environmental Forensics*, **2001**, *2*, 61-74.

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Grange, A.H.; Brumley, W.C. "Plotting Mass Peak Profiles from Selected Ion Recording Data" *Rapid Comm. in Mass Spectrom.* **1992**, *6*, 68-70.

ICE Posters at http://www.epa.gov/nerlesd1/chemistry/ecb-posters.htm

Well Pollutants Identified With A New Mass Spectrometric Technique

Ion Composition Elucidation (ICE) of Ions from Trace Levels of Pharmaceuticals and Disinfection Byproducts in Water Supplies

Characterizing Hazardous Waste Constituents: A New Tool

Identification of Analytically Problematic Pollutants with a New Mass Spectrometric Technique

Mass Determination of Intact a-Chain Hemoglobin Adducts to within 0.2 Da Using MPPSIRD with Electrospray Ionization

Deconvoluting Overlapping Isotopic Patterns Using Mass Peak Profiling from Selected Ion Recording Data (MPP[illegible]

Determination of Elemental Compositions by High Resolution Mass Spectrometry without Mass Calibrants

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