STANDARD OPERATING PROCEDURES

TRACE ATMOSPHERIC GAS ANALYZER (TAGA) IIE OPERATION

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1.0 SCOPE AND APPLICATION

The Perkin-Elmer SCIEX API 365 mass spectrometer/mass spectrometer (MS/MS) was converted by ECA into the Trace Atmospheric Gas Analyzer (TAGA) IIe to perform real-time, direct-air monitoring in both mobile and stationary modes. The TAGA is mounted in a Blue Bird bus providing instrument mobility. The layout and arrangement of one of the TAGA IIe instruments and its associated equipments are provided in Appendix A.

The purpose of this document is to describe procedures on the use of the TAGA IIe MS/MS for analysis of various targeted compounds. A list of the compounds for which TAGA analytical methods have been developed and class compounds that can be monitored/analyzed by the TAGA is presented in the MRM Table (Table 1, Appendix B TAGA analytical methods have been developed which allows the monitoring of ambient/indoor air at the parts per trillion by volume (pptv) concentrations.

The data generated using this standard operation procedure (SOP) meets the Screening Data Objective for a quick, preliminary assessment of site contamination, and provides analyte identification and quantification. The TAGA has been used to provide mass spectral information for determining the molecular structure and/or the identity of volatile organic compounds (VOCs), to isolate ambient and/or indoor sources for targeted compounds, and the rapid analysis of samples collected in Tedlar bags for VOCs.

This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometer/mass spectrometer, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 METHOD SUMMARY

The electronics are powered on and the quadrupoles are scanned for a prescribed period to stabilize the TAGA system. A standard gas mixture (e.g., trichloroethene, tetrachloroethene, benzene, toluene, and xylenes) is introduced by a mass flow controller into the sample air stream to optimize the electronic tuning, peak width and mass assignment for sensitivity and mass assignment.

A standard gas mixture containing the target compounds is introduced into the TAGA sample air stream by either a mass flow controller or an adjustable speed syringe pump dispenser. Six different concentration levels (0, 10, 20, 40, 80, and 90) are acquired during the calibration acquisition. Response factors in ion counts per second per part per billion by volume (ICPS/ppbv) are generated and used to calculate the concentration of the target compounds in ambient air samples.

Monitoring is performed by continuously drawing sample into an air stream at a flow-rate of approximately 1,500 milliliter per second (mL/sec). For the low pressure chemical ionization (LPCI) source, the air is passed through a glass splitter where the pressure gradient between the mass spectrometer core and the atmosphere causes a sample flow of approximately 10 milliliter per minute (mL/min) into the ionization source through a heated transfer line. The flow into the TAGA source is controlled so that the ionization source pressure is maintained at an optimum value (1 to 3 Torr). The remaining air flow is drawn through the air pump and vented from the mobile laboratory. For the atmospheric pressure chemical ionization (APCI) source, the entire inlet air flow passes through the ionization source. MS/MS analysis may be in the positive or negative ion mode depending on the compounds of interest.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The TAGA is generally used as a real-time monitoring instrument, providing real time screening data related to an air stream pulled past or through the TAGA's ionization source. The TAGA may also be used to analyze discrete samples collected in Tedlar bags. Pre-baked Tedlar bags must be used to collect soil gas and air samples. The presence of volatile compounds used during the manufacturing of Tedlar bags will rapidly contaminate the TAGA ionization source and drastically reduce instrument response in as little as three analyses.

3.1 Sample Storage

Samples collected in Tedlar bags should be placed in a clean and cool environment (at room temperature) out of direct sunlight to prevent photodegradation. The bag samples should arrive at the mobile laboratory with the valve closed and an identification tag attached.

3.2 Holding Times

For best results, samples should be analyzed within the first 12 hours of collection. Samples must be analyzed within 24 to 48 hours after collection.

Samples may be recorded on a chain of custody (COC) record (optional for screening locations) indicating sampling locations, sample numbers, date collected, sample matrix, and sample volumes. The COC record should agree with the information on the Tedlar bag labels and discrepancies should be noted on the COC record at the time of receipt by the mobile laboratory. In addition, any obvious physical damage or contamination (e.g., broken valves, condensate in the bag, or bags being flat) should also be recorded on the COC record.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

- The four basic types of interferences that can cause ambiguity in the results are: 1) ionization mechanism, 2) structural isomerization, 3) water or nitrogen oxide (NOx) clustering, and 4) formation of the target substance in the ionization source.
- Highly polar compounds with high molecular weights demonstrate lower transport efficiency due to interaction with the surface of the Teflon hose. The severity of this effect is partially dependent on the ambient air temperature.

5.0 EQUIPMENT/APPARATUS

- TAGA IIe MS/MS system equipped with standard data collection and manipulation software.
- Additional Macintosh G3/G4 for data reduction.
- A Macintosh G3/G4 compatible printer and graphic computer display terminals.
- Multipurpose APCI source consisting of digitally controlled corona discharge ionizer and associated power supplies
- LPCI source and associated digital hardware control components
- Direct atmospheric sampling inlet (transfer line) for LPCI source and all associated plumbing
- MKS mass flow controllers, range 0-10, 0-100, and 0-100,000 standard cubic centimeter per minute (sccm)

- MKS Type 146 Digital Vacuum Gauge Measurement and Control System
- Varian ConvecTorr analog pressure meter
- Bertan Series 915 source power supply
- Harvard PHD 2200 Infusion Syringe Pump (Harvard Apparatus, Inc. or equivalent)
- Glass Splitter for LPCI source inlet (Ace Glass, or equivalent)
- Teflon® hose, convoluted or corrugated (approx. 1.1" OD and 0.85" ID) of lengths varying from 12 inches to 300 feet
- Polypropene hose, convoluted or corrugated (approx. 1.1" OD and 0.85" ID) of lengths varying from 12 inches to 20 feet

6.0 REAGENTS

- Ultra-pure Nitrogen (99.999% or better) - curtain gas and collision gas, carrier gas for syringe pump and impingers
- Gas standard (certified at ±2% accuracy) - calibration materials
- Liquid phase standard (certified 99% pure or better) - calibration materials
- Solid phase standard (certified 99% pure or better) - calibration materials
- Methanol - ACS Grade - cleaning solvent
- 2,2,5-trimethylpentane (isooctane) - ACS grade - cleaning solvent
- Propionic, butyric, valeric, heptanoic, octanoic and nonanoic acids.
- Diethyl Malonate
- Diisopropylmethylphosphonate (DIMP)
- Benzene
- Tributylphosphate
- Acetone
- Methylethylketone (MEK)
- Methylisobutylketone (MIBK)

7.0 PROCEDURES

The TAGA IIe can be operated with the LPCI source in either positive ion or negative ion mode and with the APCI source in either positive ion or negative ion mode. The predominant mode of operation is LPCI in positive ion mode, and daily procedures are written for that mode. Operational procedures or procedural variations specific to the other modes of operation are discussed in other sections.

7.1 TAGA IIe Pump Down and Warm-Up

This part of the procedure assumes that the system is completely shut off, and the vacuum system of the TAGA is at atmospheric pressure. If the TAGA vacuum system is on, then start at step 5. Refer to Appendix A for pictures of the TAGA IIe and various components discussed here.

1) Check that there is nitrogen supply and the cylinder is open (Appendix A, Pictures 1 and 2). Ensure that the pressure regulator is set between 20 to 40 pounds per square inch (psig). Optimal pressure setting will vary from instrument to instrument. The TAGA turbomolecular pumps will not start unless there is adequate supply gas pressure. Also, if the nitrogen line pressure is too high, the amount of nitrogen flow into the vacuum system during pump-down

will prevent the system from achieving the necessary degree of vacuum to operate.

2) Use the three toggle power switches (Appendix A, Pictures 3 and 4), located inside or outside of rough pumps area, to pump down the instrument. Turn on one rough pump. Wait about 15-seconds, and then turn on the second rough pump. If using the LPCI source, ensure that the source pressure controller (Appendix A, Picture 5) is in place and its rough pump (Appendix A, Picture 7) is turned on.
3) **Wait at least five minutes before turning on the TAGA (turbo switch).** This allows the rough pumps to create sufficient vacuum prior to operating the turbomolecular pumps, which are designed to be turned on after the rough pumps have done their job. With an insufficient vacuum generated, the turbomolecular pumps will not achieve operating speed within the required time and be timed out in order to protect the turbomolecular pumps from damage.
4) Toggle on the TAGA (Turbo) Power switch (Appendix A, Picture 4). This powers up the TAGA and simultaneously starts the turbomolecular pumps. While the TAGA is starting up, the green status light, (Appendix A, Picture 2) should be flashing. If the green light does not flash, check that nitrogen is set at an appropriate pressure and is being supplied. When full operational status is achieved (in approximately five minutes), the green light is on continuously.
5) While waiting for the TAGA to achieve full operating status, check to see if the GPIB interface box (located under the operator's desk) is on. If it is not on, turn on the interface box.
6) Turn on the computer by depressing the power button on the front of the computer. It takes a few minutes for the computer to boot up, so be patient. **Note: The TAGA will maintain a very high nitrogen usage until the computer is turned on and the Tune program is loaded. <u>If the TAGA is turned on, and Tune is not loaded, an entire cylinder of nitrogen may be consumed over an eight to twelve hour period.</u>**
7) After the computer is on, and has completed its starting dialog, the opening screen (Figure 7.1.1) appears.

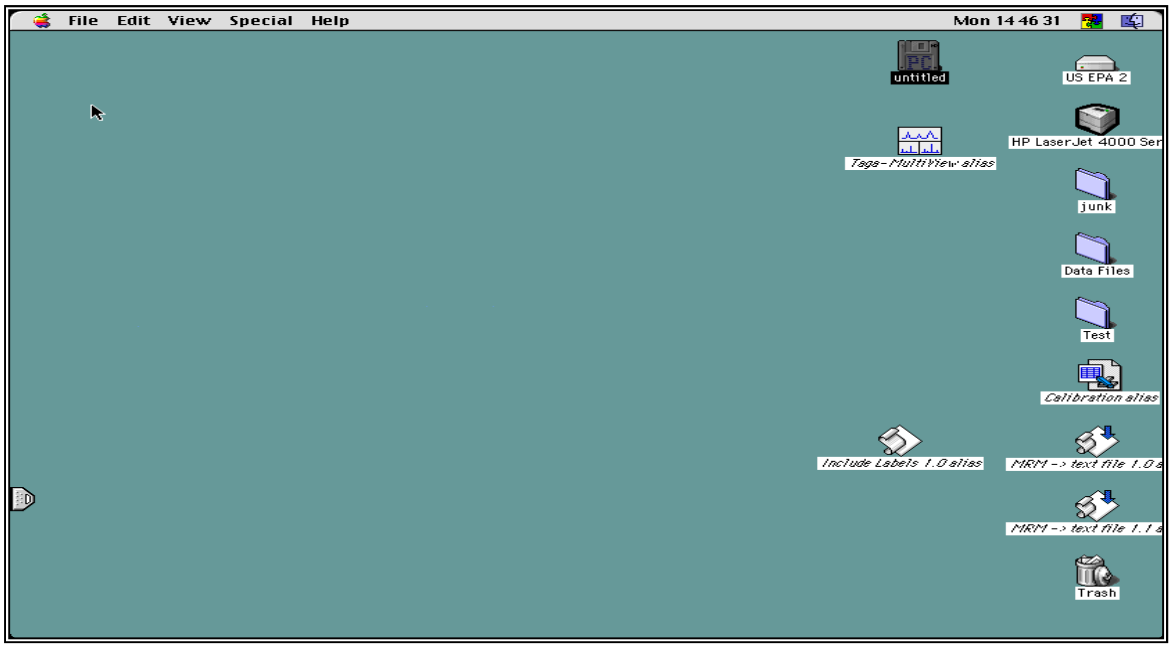

Figure 7.1.1 Initial Computer Screen

8) Check the day-month-year and time on the computer, update if necessary. Set the time to the nearest second. To set date and time set, click on the Apple icon in the menu bar → Control Panel → Date and Time (Figure 7.1.2)

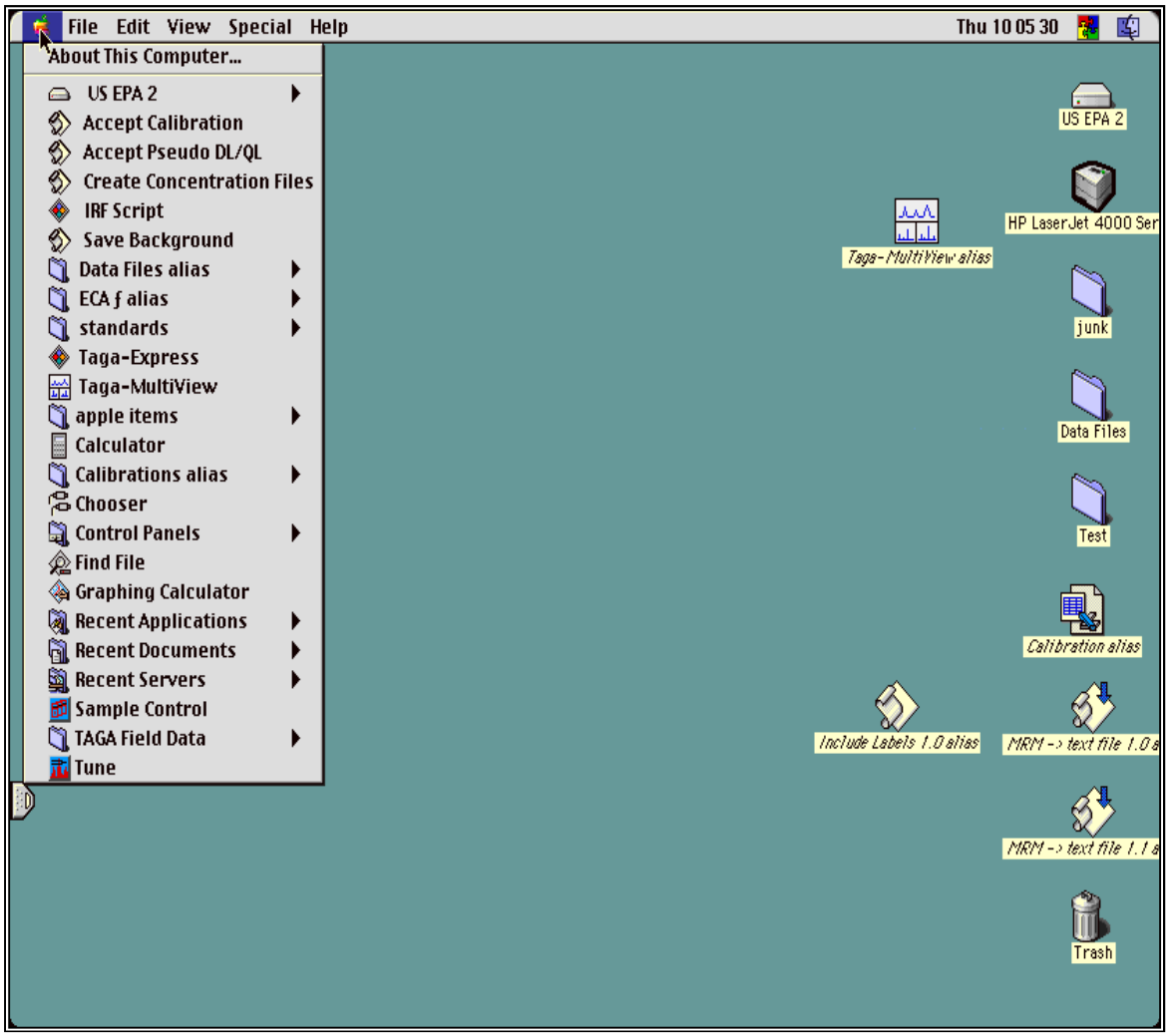

Figure 7.1.2 Main Menu Selections

9) Click on the Apple icon in the upper left corner of the screen, select [TUNE] from menu selection to open the TUNE screen (Figure 7.1.3).

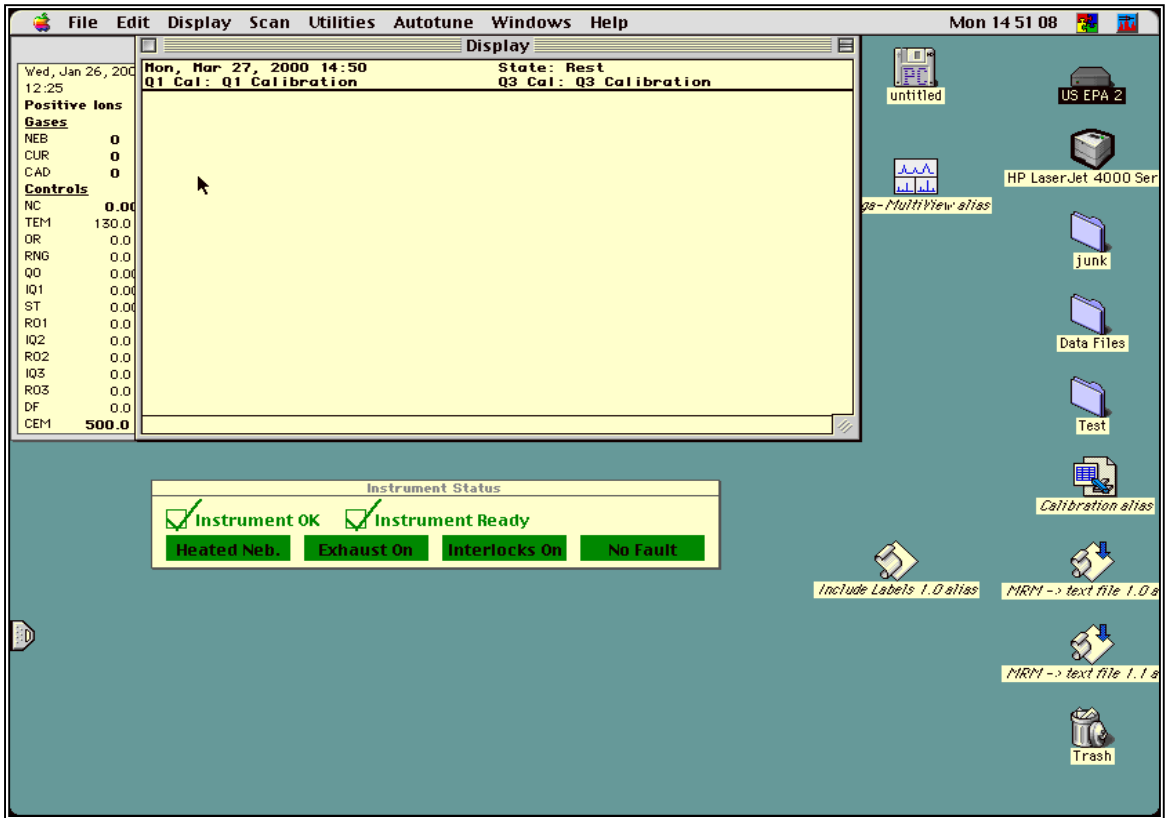

Figure 7.1.3 Initial TUNE Screen

In the display pane, the state file should be "Rest"; the last selected state file before the computer is turned off will be retained. If not, at the menu bar, select [FILE] [OPEN STATE FILE], choose "Rest" → [Open].

10) Click on the Instrument Status pane. On the menu bar, select [OPTIONS] [DETAILED STATUS]. The operational status of the vacuum system will be displayed. Wait until the Instrument Ready box is checked in the Instrument Status pane, and in the green as above. The instrument status will change to READY once the internal pressure has registered less than 5.0×10^{-5} Torr for three consecutive readings. When the instrument has been pumping down over night, the vacuum reading in the Detailed Status box should be about 0.2×10^{-5} Torr.

11) This step is generally not needed, since the settings are saved in permanent memory, but should be checked to be sure, there have not been any changes. Click on the display pane, then on the menu bar select [EDIT] [PARK MASS PARAMETERS]. Set the park masses for Q1 and Q3 to 150.00 (factory settings are 1400.00) → OK.

12) At the MKS Type 146 Control System (MKS box), (Appendix A, Picture 11) press ON → 3. This will power on the sample air flow (SAF) controller, which should be connected to channel 3 on the MKS and set for 1,500 mL/sec. Refer to Appendix D for MKS instructions.

Detach Teflon hose from glass splitter and ensure that air is being drawn through the hose. There are two blowers installed and it is possible for the MKS box to indicate air flow is present when no air is being drawn through the hose.

13) Verify that the Teflon tubing from the selected calibration gas cylinder is connected to a mass flow controller (MFC) and channel #1 at the MKS box. Attach the other end of tubing to the glass splitter (Appendix A, Picture 8).
14) Set the output pressure of the calibration gas cylinder between 20 to 40 psig. Open cylinder valve.
15) Using the needle valve underneath the LPCI source (Appendix A, Picture 6) slowly open the valve allowing flow into the source. Monitor source pressure at the Varian ConvecTorr Analog Pressure Meter (Appendix A, Picture 10). (Examples of typical setting are: Bus 1553 at about 1.2 Torr and Bus 1693 at about 2.5 Torr.)
16) Adjust the source pressure between 1.0 Torr to 3.0 Torr. The optimum pressure will vary depending on which target compounds are selected and the absolute humidity.
17) Check to be sure the high voltage cable from behind the Bertan Series 915 is attached to the electrode in the LPCI source.
18) Power on the Bertan Series 915 (source power supply) (Appendix A, Picture 9), and set current to 25 micro amp (µA). Setting will vary. **Note**: the two toggle switches on the Bertan 915 must be in the up position for current to flow to the electrode. If the current is regulating properly, the 'voltage' light on the lower left of the front panel of the Bertan 915 will be off, and the 'current' light on the lower right will be on. It may be necessary to adjust the source pressure to get the 'voltage' light to turn off, and the 'current' light to turn on.
19) At the computer → menu bar → [FILE] [OPEN STATE FILE], choose the most recent state file or other desired state file → [OPEN]. The selected state file will set the various TAGA voltages previously used. **Note:** the state file includes the CEM voltage, and that voltage may be incorrect for the condition of the CEM currently in use. If the voltage is too high, this will cause reduced CEM life. If the voltage is too low, no ions may be detected.
20) At the menu bar, select [FILE] [SAVE STATE FILE AS]. General state file name format is as follows: "Year Month Date Mode Compound Identifier". Example: "2008 Dec 18 LPCI PCE - TCE"
21) At the menu bar, select [FILE] [OPEN EXPERIMENT FILE] → choose an experiment file appropriate for the task, ex. "develop" → [OPEN]. As seen in Figure 7.1.4, this selects an experiment that displays ion pairs for a selection of aromatic and chlorinated organics. **IMPORTANT: The Experiment Editor under TUNE can use a maximum of eight ion pairs. The icon for the Experiment file created under TUNE is an outline, while the Experiment icon created under SAMPLE CONTROL is a filled-in color icon. An Experiment created under SAMPLE CONTROL can be opened under TUNE, however, only the first eight ion pairs will be included. Be careful not to save a Sample Control created Experiment while in TUNE; all of the ion pairs after the first eight will be permanently lost.**

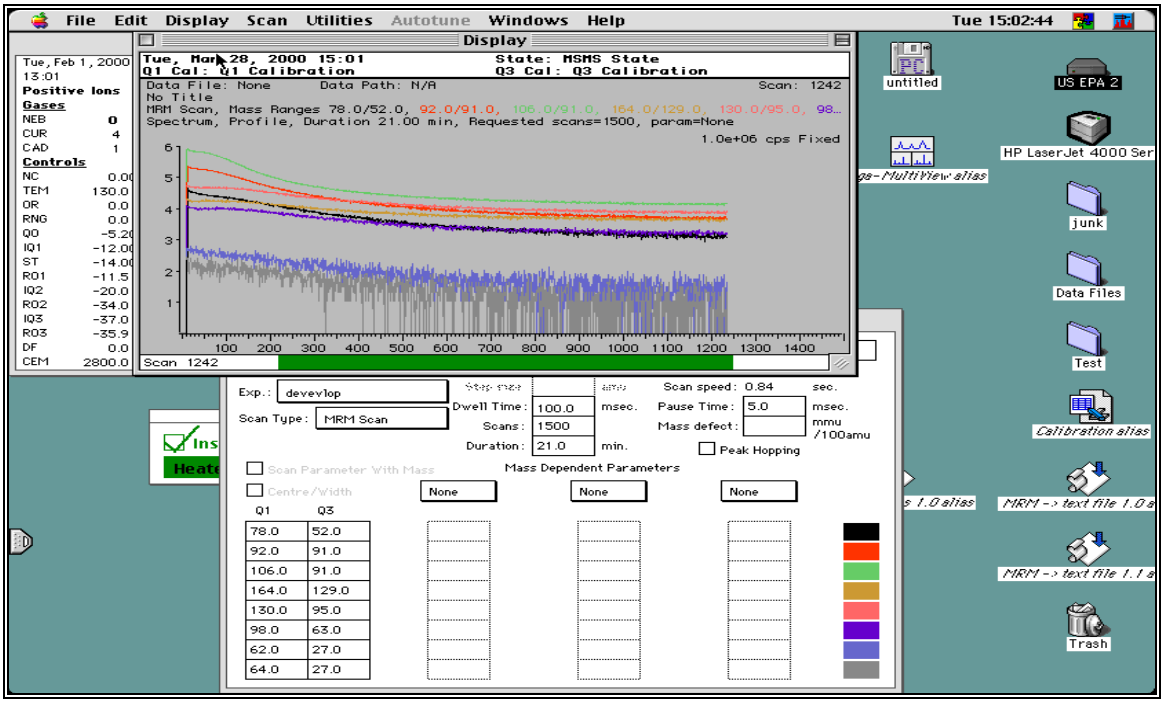

Figure 7.1.4 Warm-Up Trace, Charging Due to Dirty Source

22) At menu bar, select [DISPLAY] [LOGARITHMIC]. Double click on the range to set.
23) At menu bar, select [SCAN] [START]. The instrument will start scanning the selected ion pairs. Allow to acquire for about 10 to 15 minutes if unit was started from a vented position. (Figure 7.1.4)
24) Menu bar →[SCAN] [FINISH]
25) Instrument is now warmed-up electronically.
26) At this point a system shut down may be performed (section 7.2) or can proceed to tuning the instrument and readying for analysis (section 7.3).

7.2 TAGA IIe End of Day Shut Down

It is important to understand that the TAGA electronics remain in the last state sent by the computer, whether or not the computer is on. Therefore, the TAGA must **always** be placed in the REST state prior to turning off the computer.

1) Close out of all active software, except for MacDAD. Click at the upper right hand corner of the menu bar to see which applications are still running. Close each application individually.
2) Menu bar → Apple icon → [TUNE].
3) Menu bar → [FILE] [OPEN STATE FILE].
4) Select [REST] → [OPEN]. This puts the TAGA electronics in the Rest State.
5) Menu bar → [FILE] [QUIT]. This quits out of TUNE.
6) Menu bar → [FILE] [QUIT]. This quits out of MacDAD.
7) Menu bar → [SPECIAL] [SHUT DOWN]. **Note:** The computer tends to accumulate errors

while operating; it is strongly advised that it be shut down completely at the end of each operating day.

8) Use the front panel controls of the MKS box (Appendix A, Picture11) to turn off the flow controllers that are in use. (OFF, 1; OFF, 2; OFF, 3; OFF, 4).
9) Close any calibration gas cylinder opened during operation.
10) Shut off the source power supply (Appendix A, Picture 9). **Do this before reducing the source pressure with the needle valve. The power supply provides a constant current, and can produce voltages as high as 5000 volts (V).** Normal operating voltage at the proper source pressure is around 350V.
11) Reduce source pressure to under 0.1 Torr. **THE NEEDLE VALVE IS NOT DESIGNED FOR SHUT OFF SERVICE.** Be very careful to avoid using the needle valve as a shut off valve. The knob of the needle valve should be adjusted to make complete shut-off impossible.

7.3 Tuning the Instrument

The TAGA's SCIEX APCI 365 manual contains extensive information on the structure and operation of the various elements within the instrument. This section assumes a fundamental familiarity with the manual, and provides a minimal description of the basic tuning process for the LPCI source. Additional tuning guidelines are provided in Appendix C for both the LPCI and APCI source. For the purposes of this procedure, it is assumed that the mass assignments and resolution are reasonable and correct. This will normally be the case.

1) Turn on and warm up the instrument as in Section 7.1.
2) At the menu bar, select [FILE] [OPEN EXPERIMENT FILE] → choose an appropriate Experiment for the job at hand. For instance if the day's work will be to monitor for tetrachloroethene (PCE) and trichloroethene (TCE), select Experiment PCE+TCE.
3) **Important:** Make sure to save the State File as in step 19 of section 7.1 before continuing.
4) **Turn on the appropriate standard gas cylinder, set the pressure to between 20 and 40 psi, and make sure the valve on the regulator is open, supplying gas pressure to MFC one.**
5) At the MKS box (Appendix A, Picture 11), depress ON → 1. Make sure display is set to 90, if not see section Appendix D for MKS instructions. This allows 90 mL/min of the calibration gas to mix with air from the SAF at 1500 mL/sec resulting in a 1000: 1 dilution at the inlet of the TAGA. Therefore, a compound present at 20 parts per million by volume (ppmv) in the standard will have a concentration of 20 ppbv at the TAGA inlet.
6) At menu bar, select [DISPLAY] [LOGARITHMIC]. Double click on the range to set.
7) At menu bar, select [SCAN] [START].
8) Using the needle valve, optimize the source pressure by opening the valve in small increments. Using both the Varian analog meter and the computer screen, determine the pressure that provides the highest response. (Figure 7.3.1)
9) Increase the pressure by approximately 0.2 to 0.4 Torr. Then turn on the source pressure controller at the MKS box, ON → 4.
10) If needed, refer to Appendix D to adjust the pressure setting of the MKS box, so that the pressure on the analog gauge is the same as determined during pressure optimization.
11) Optimize the multiplier voltage; while scanning, click on to the CEM voltage in the State File window (right side of screen), and increase it by 50 volts. If the signal increases significantly,

repeat the process. If the signal doesn't increase significantly, return the voltage to its previous value.

12) Optimize the collision gas pressure; change the curtain gas (CUR) and collision gas (CAD) settings to maximize the signal. Fine control can be achieved by varying the nitrogen supply pressure. Typically, the optimum CAD setting will be around 3 or 4, and the pressure will read around 2.8 x 10^{-5}.
13) At the menu bar → [FILE] [PRINT] [PRINT]. This will document your starting point.

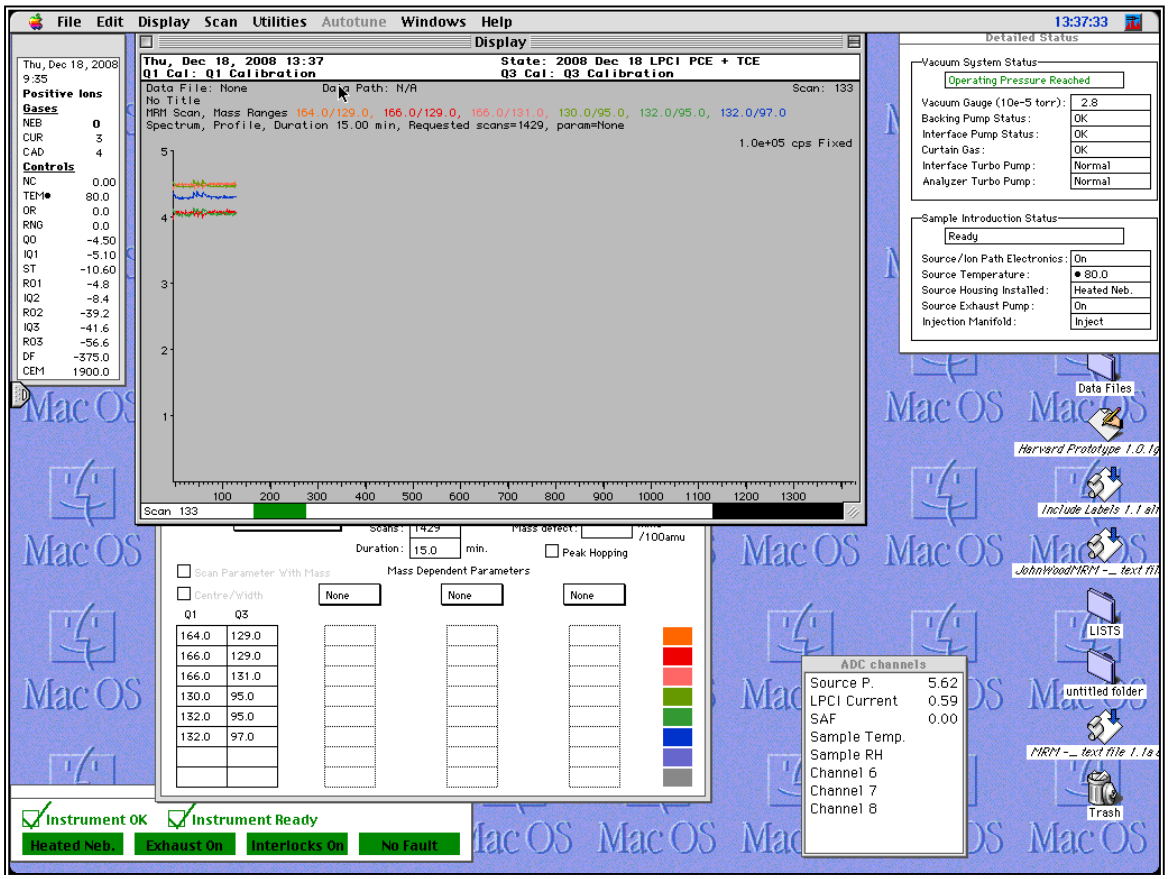

Figure 7.3.1 Establishing Starting Ion Intensities

14) Menu bar → [SCAN] [FINISH].
15) Sequentially optimize voltages for each parameter.
16) Menu bar → [SCAN], [EDIT PARAMETER SCAN] (Figure 7.3.2)

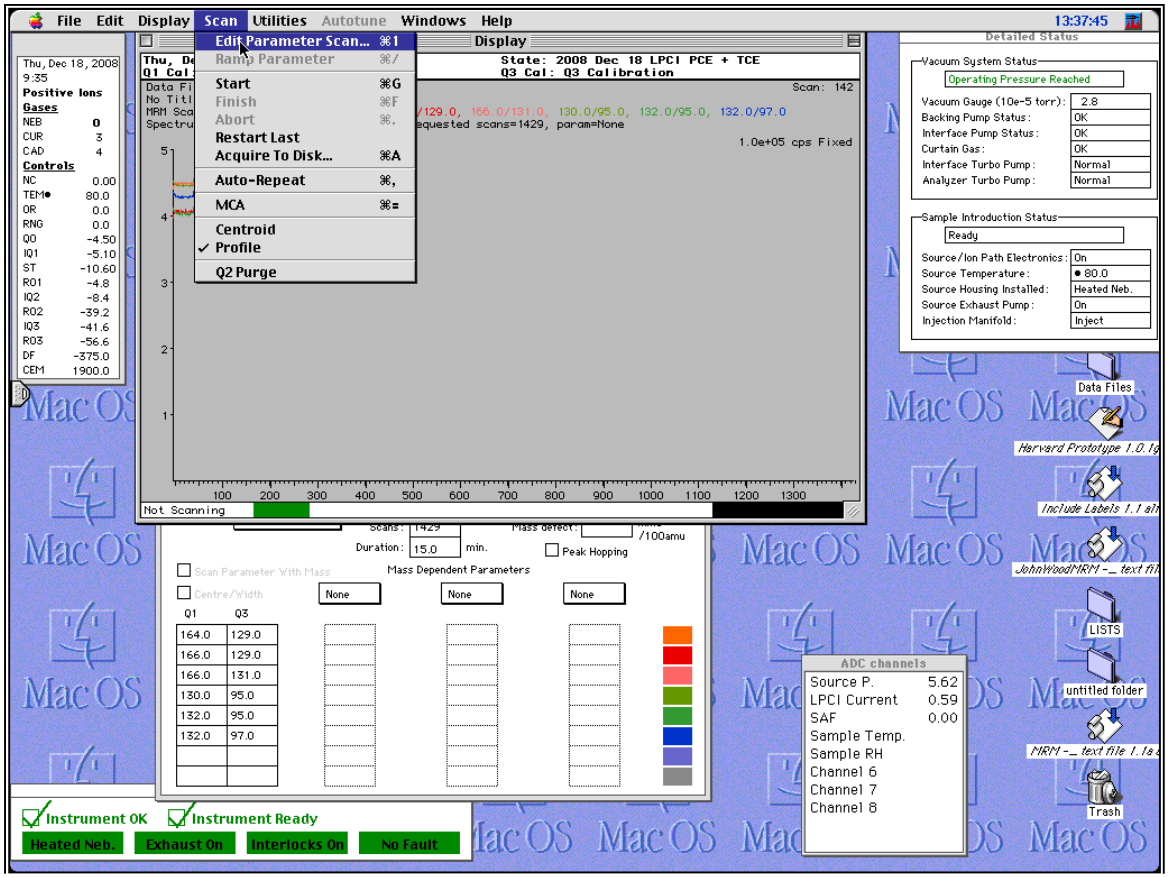

Figure 7.3.2 Preparing to Edit State File Parameters

17) Refer to Appendix C for recommended parameter ranges.

18) First select Q0, and set the appropriate voltage range of values through which the instrument will scan (Figure 7.3.3).

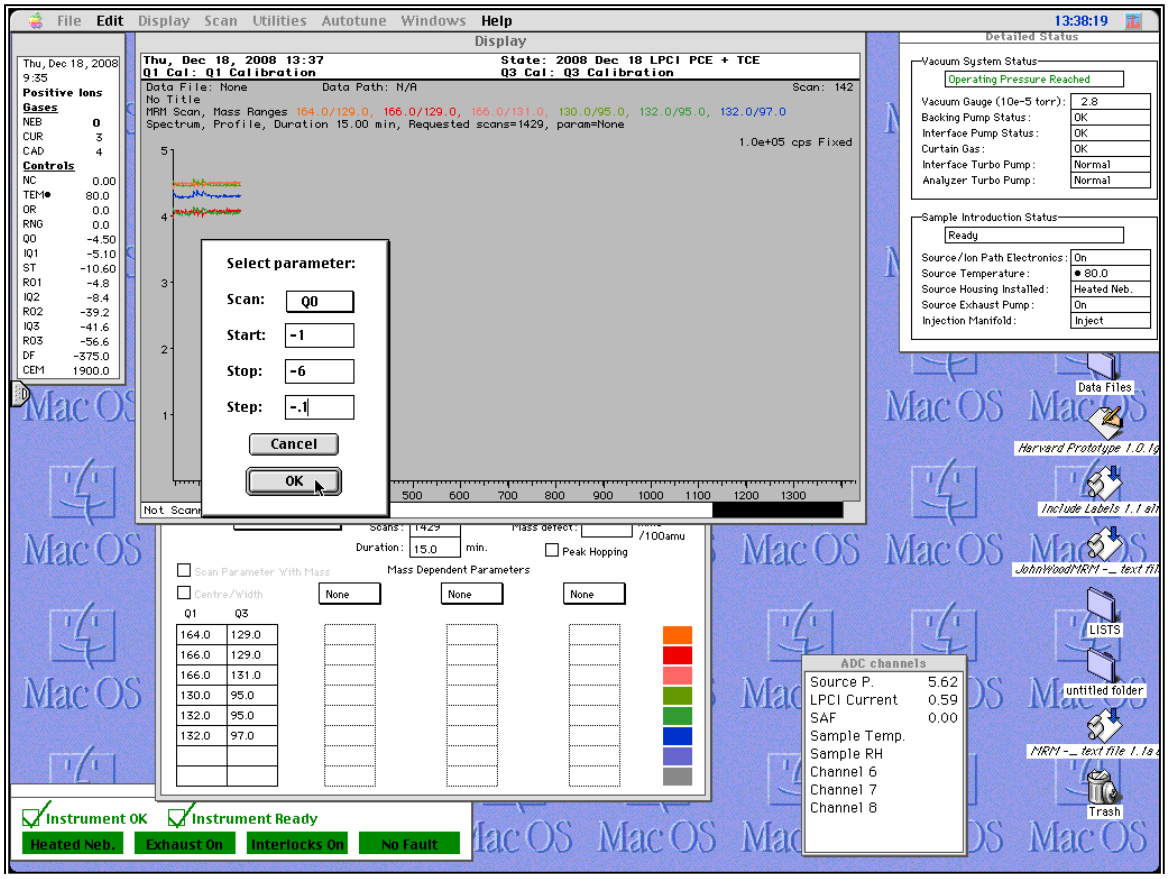

Figure 7.3.3 Entering Parameters to Scan

19) For example: for Q0 in the positive ion mode; Start: -1 → Stop: -6 → Step: -0.1, as shown in Figure 7.3.3. Click → [OK].

20) At the menu bar → [SCAN], (note that the Ramp Parameter is now checked), [START] (Figure 7.3.4).

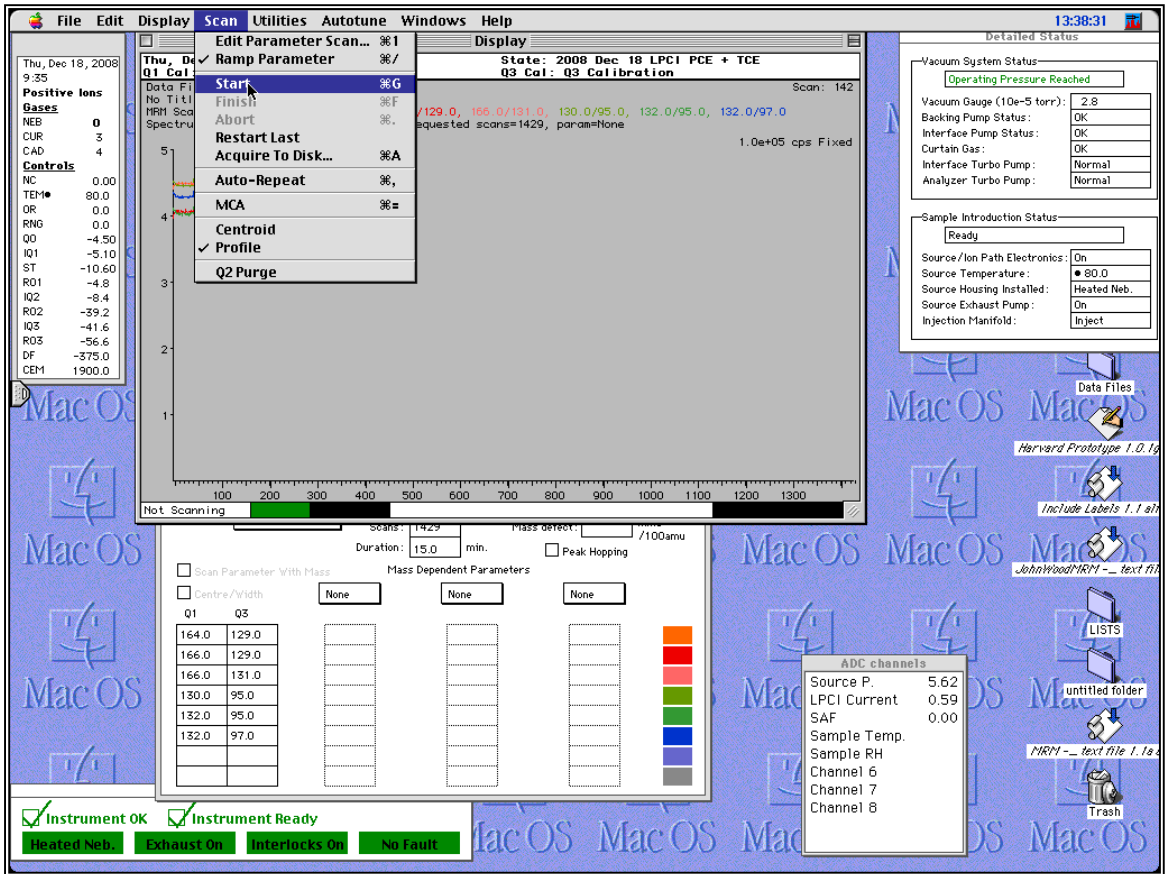

Figure 7.3.4 Starting to Scan Parameter

21) Once the parameter scan has been completed, select the maximum output in a reasonably flat zone and double click that point (Figure 7.3.5). This will change the value in the State File to the selected value. Note that the maximum may be at different voltages for different ion pairs. At times a judgment call must be made based on which compound(s) optimization is centered upon.

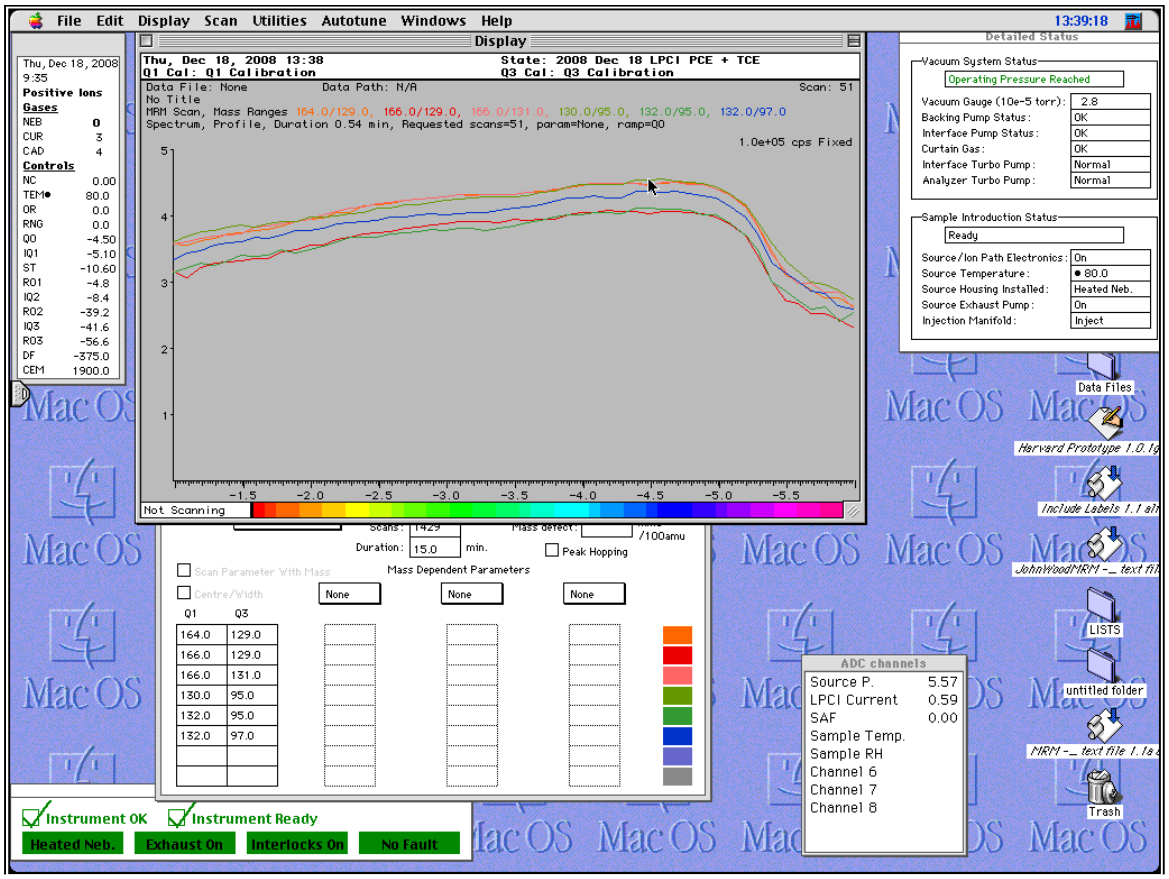

Figure 7.3.5 Completed Q0 Parameter Scan

22) Repeat the process for the rest of the parameters, through the DF, changing the ranges and step sizes as appropriate. Note that this is an iterative process, and the various parameters are interrelated.
23) For the LPCI source, optimize voltages for parameters from Q0 to DF. The LPCI source does not have an orifice plate or focusing ring, so the OR and RNG values in the State File will be zero. The APCI source, optimize voltages for parameters from OR to DF.
24) When all parameters have been optimized, at the menu bar → [EDIT PARAMETERS] Scan: → NONE → OK.

25) Menu bar → [SCAN] [START]. Collect about 100 to 200 scans, allowing the signal to stabilize.

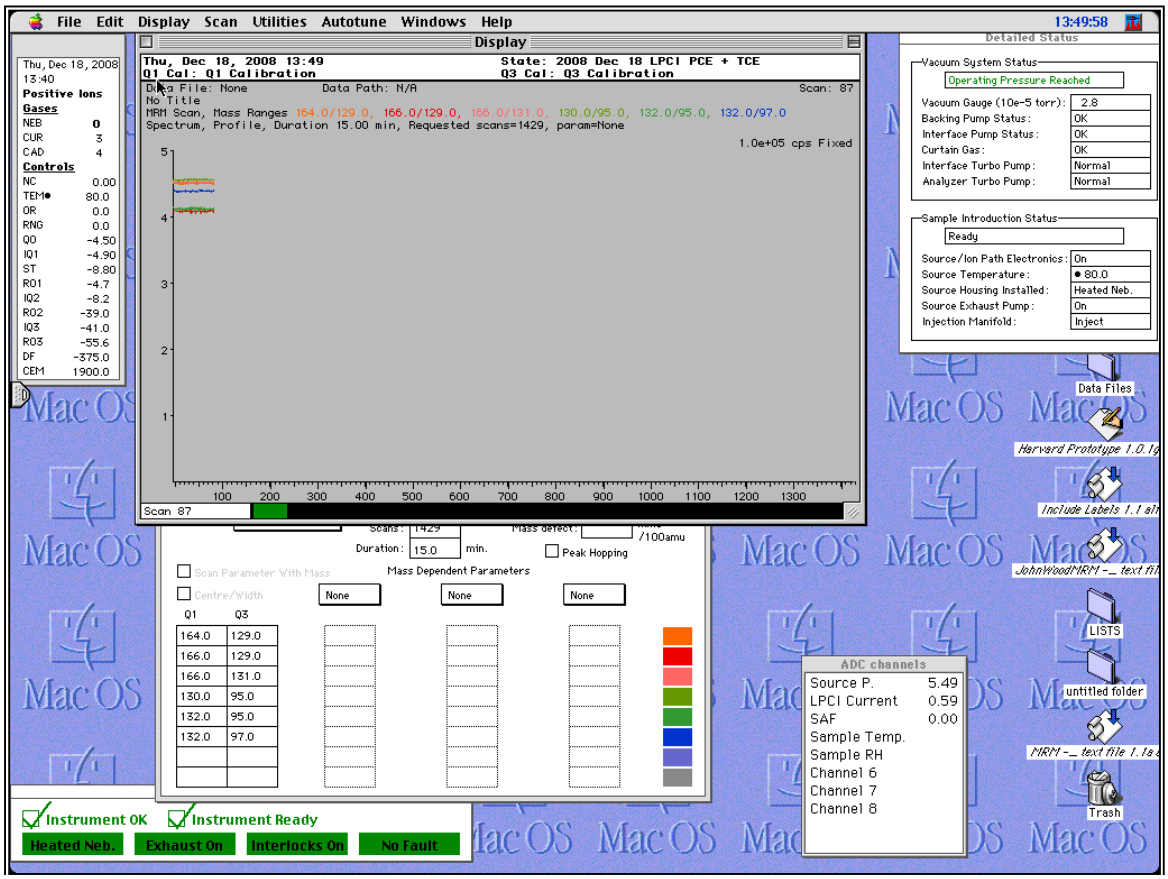

Figure 7.3.6 Scan to Demonstrate Tuning Results

26) Menu bar → [SCAN] [FINISH] [FILE] [PRINT] [PRINT]
27) Menu bar → [FILE] [SAVE STATE FILE]. Save file with current date.
28) Make visual comparison with print out from step 11.

7.4 Mass Calibration

1) Perform after completing the tuning operation in section 7.3.
2) Set the CAD gas setting to zero (usually set to 3 or 4 in the operating state file).
3) Menu bar → [FILE], [OPEN EXPERIMENT FILE].

4) Choose [LPCI Q1 READY] or appropriate experiment file. This selects an experiment that scans selected intervals from 25 to 175 atomic mass unit (amu), with a step interval of 0.1 amu (Figure 7.4.1).

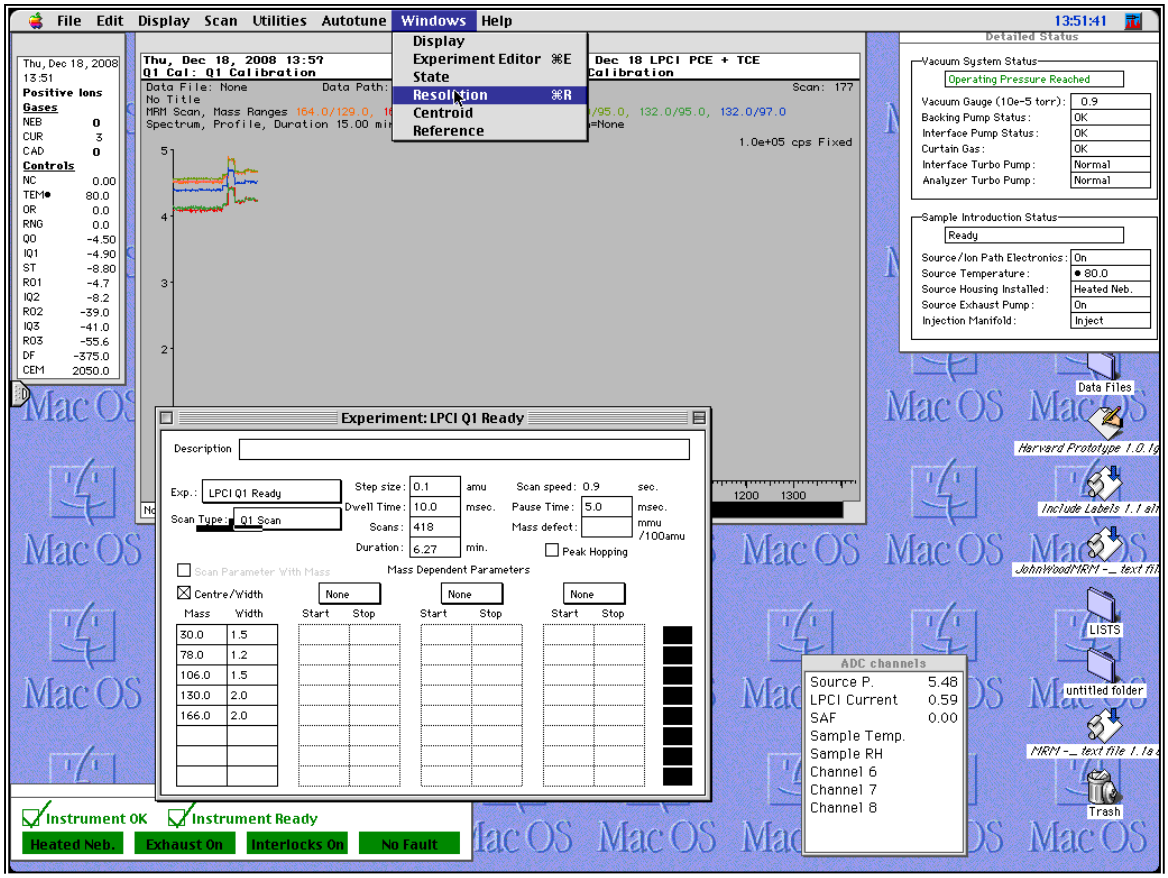

Figure 7.4.1 Selecting Resolution Window

5) Menu bar → [WINDOWS] [RESOLUTION]; [WINDOWS] [REFERENCE]. (Figure 7.4.2)
6) In the Reference screen, click on the [Select. Ref File] button to choose a Q1 m/z file. If unsure which file to use, a file can be highlighted and then click the [PEEK] button to view the m/z ions in that file. Click [DONE] to exit the peek view.

7) Choose [CALGAS#2 Q1]; click [OPEN] once selection has been made.

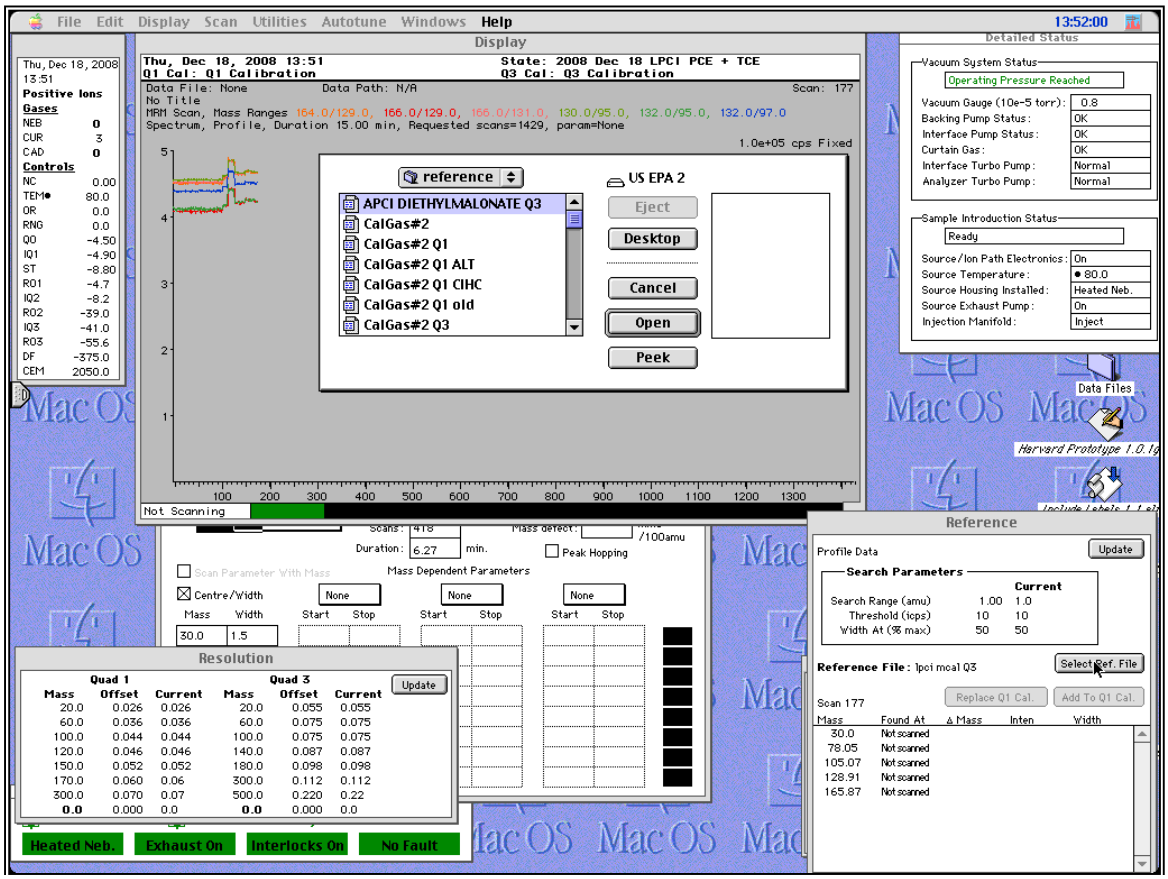

Figure 7.4.2 Selecting the Reference File

8) Click on the Display screen → menu bar → [DISPLAY] → [LINEAR].

9) Menu bar → [SCAN] [MCA] [SCAN] [START]. Allow 10 to 20 scans to be acquired. The selected peaks will now be seen as they build on the screen (see Fig. 7.4.3). Note that the values displayed in the Reference screen for each peak width and actual mass will change slightly with each scan and is an accumulated average. The purpose of the MCA is to minimize errors due to instrumental noise or minor random fluctuations in ion intensity.

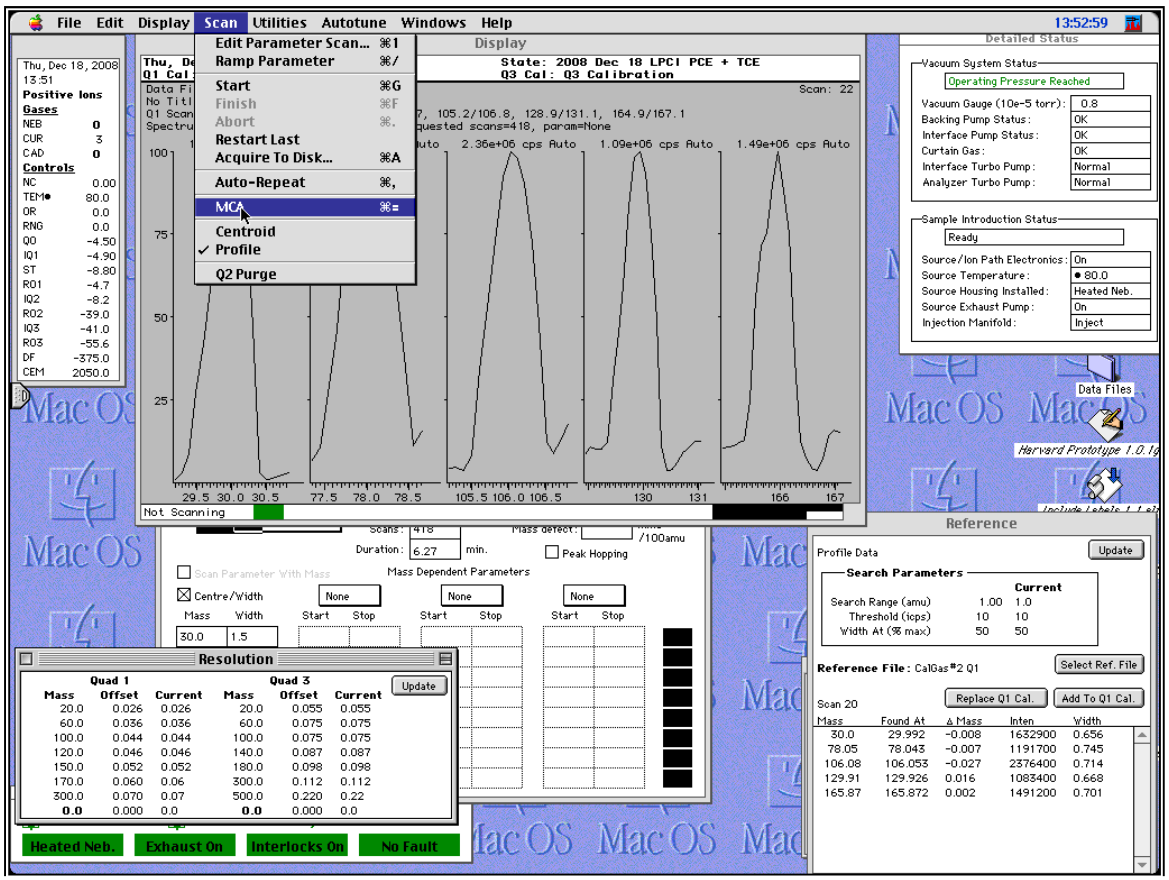

Figure 7.4.3 Selecting MCA

10) If the Δ masses are less than 0.15 amu and the peak widths are between 0.60 and 0.80 amu, the calibration is acceptable (Figure 7.4.4). Proceed to step 22.

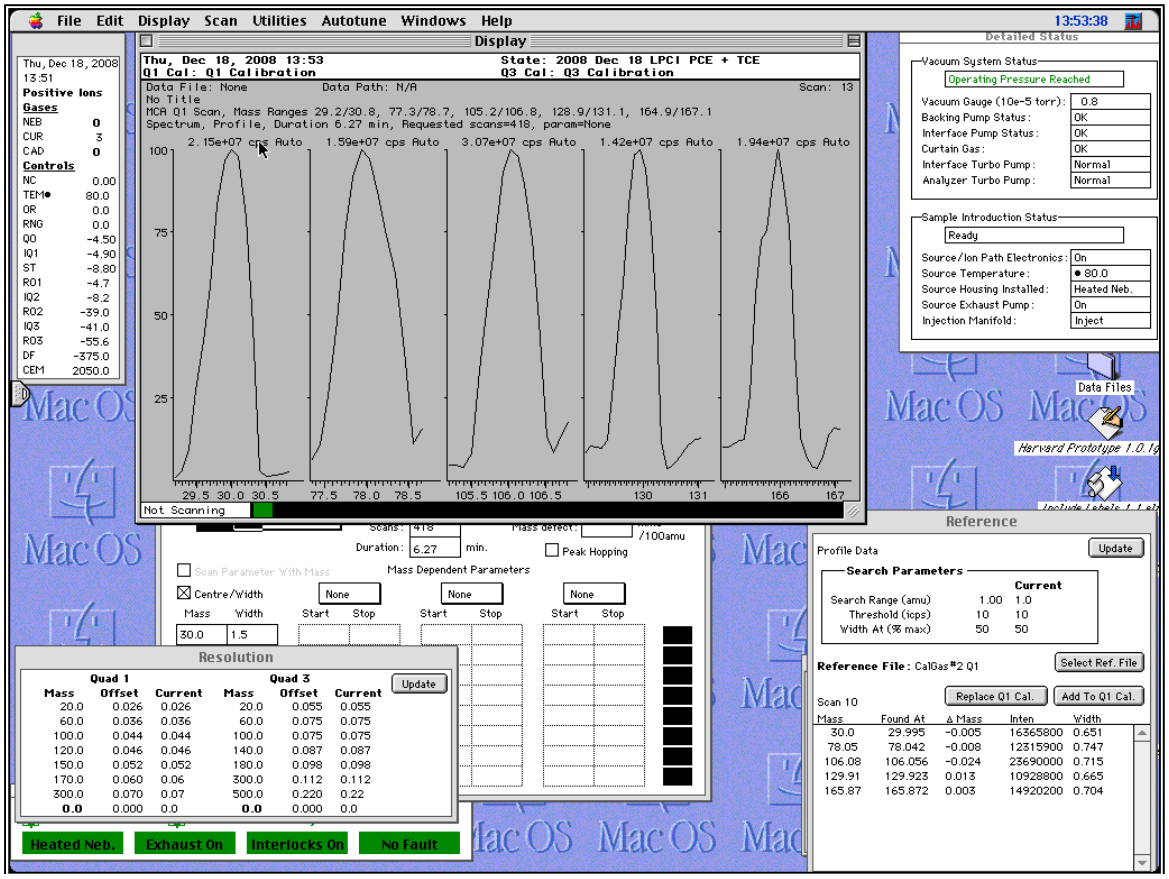

Figure 7.4.4 Averaged Q1 Resolution and Mass Assignment

11) If any of the Δ mass is greater than 0.15 amu, first be sure that the peaks are correctly assigned, and not the result of background contamination. Use a pure compound standard for verification. For this example, use a slightly opened bottle of PCE to be sure of its peak assignments, this compound is the one most likely to suffer interference. To ascertain if peak selection is correct, watch the screen for the rise and fall of the peak as the bottle is brought closer then farther from the inlet.
12) If the peak selections are correct, update the mass assignment by clicking the [UPDATE] button in the Reference screen. (Figure 7.4.5). This will reset the mass offset.

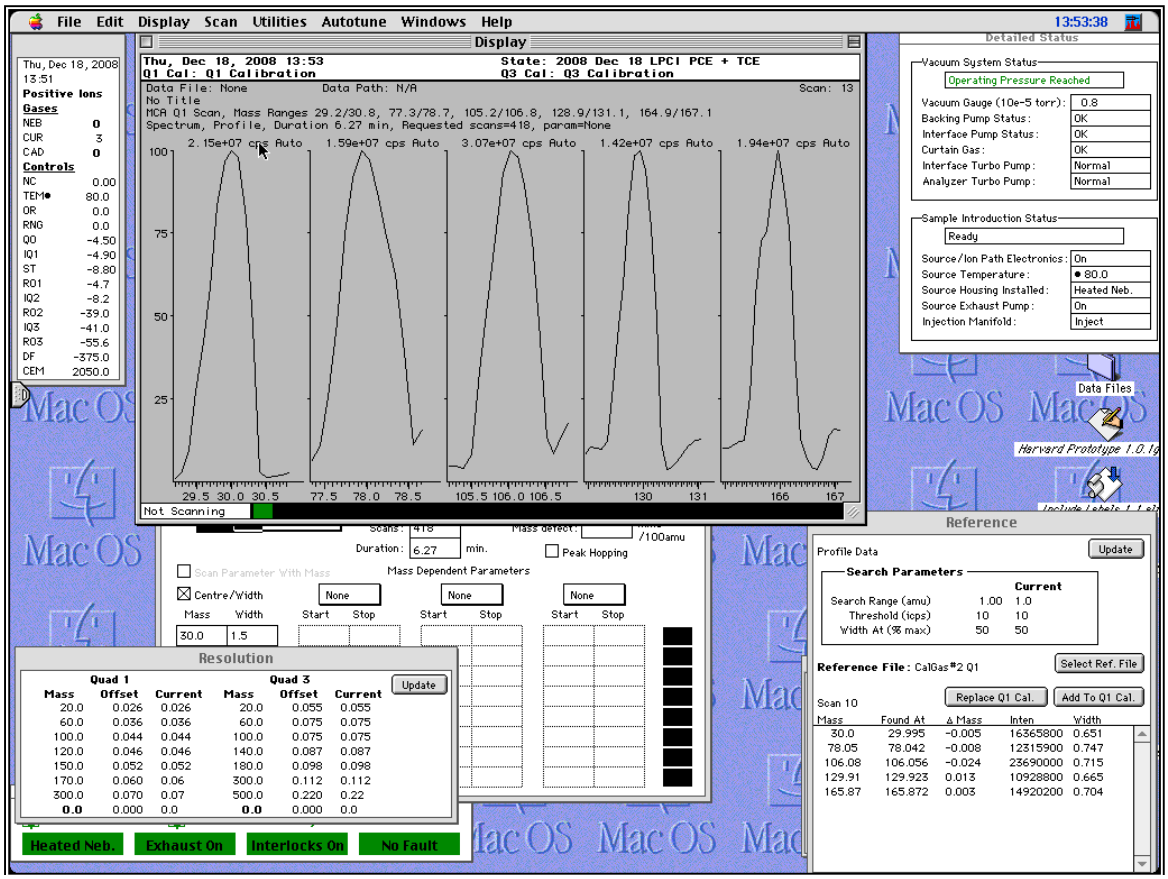

Figure 7.4.5 Updating the Q1 Mass Calibration

13) Note that the "Q1 CALIBRATION" in the upper left portion of the display (Figure 7.4.6) will be replaced by the date. This means that the temporary Q1 calibration is in use, rather than the one saved on the hard drive. **NOTE: BE SURE THAT ALL OF THE CORRECT PEAKS HAVE BEEN SELECTED. DOUBLE CHECK BEFORE GOING ON TO THE NEXT STEP**!!

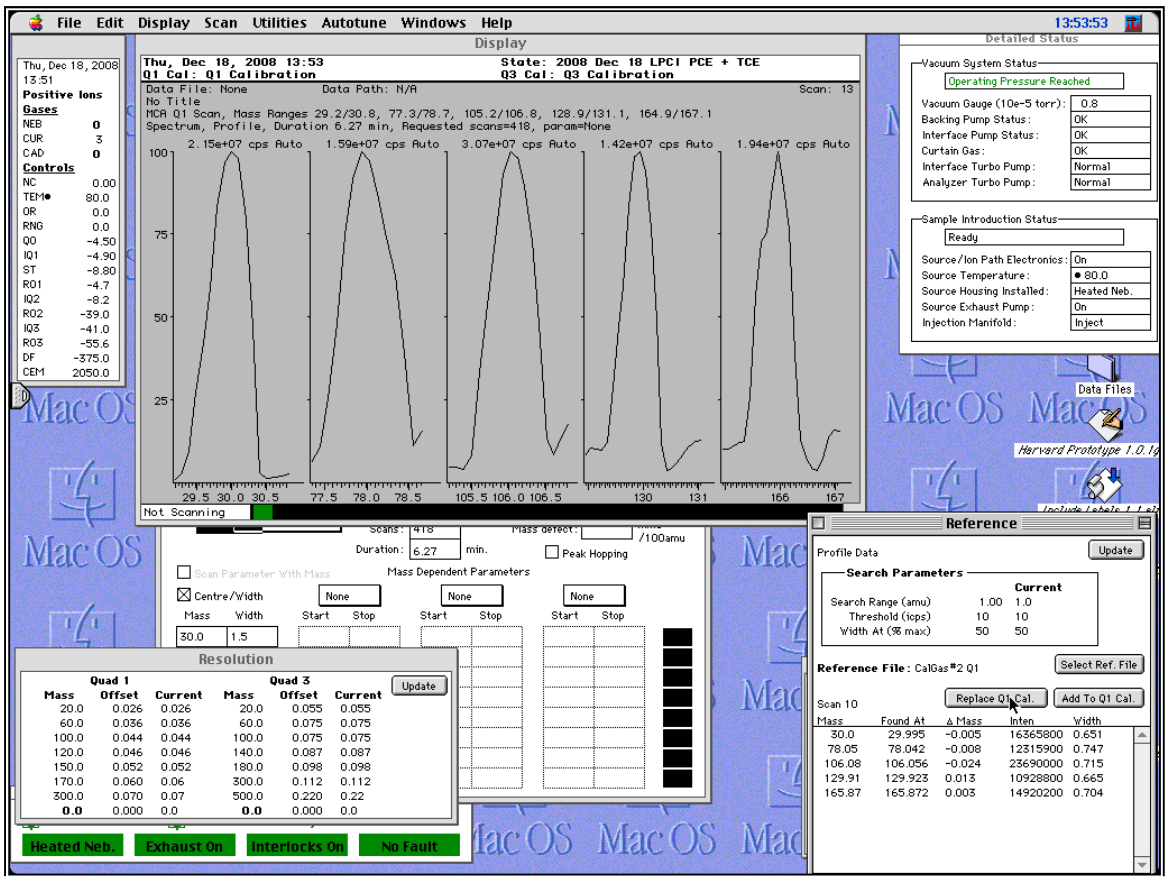

Figure 7.4.6 Prior to Date Replacing "Q1 Calibration"

14) At this point, the effect of the mass offset can be evaluated prior to replacing the Q1 Calibration file.

15) Menu bar → [FILE] [SAVE CALIBRATION AS] [Q1]. (Figure 7.4.7). **Note:** the software always defaults the location to the desktop.

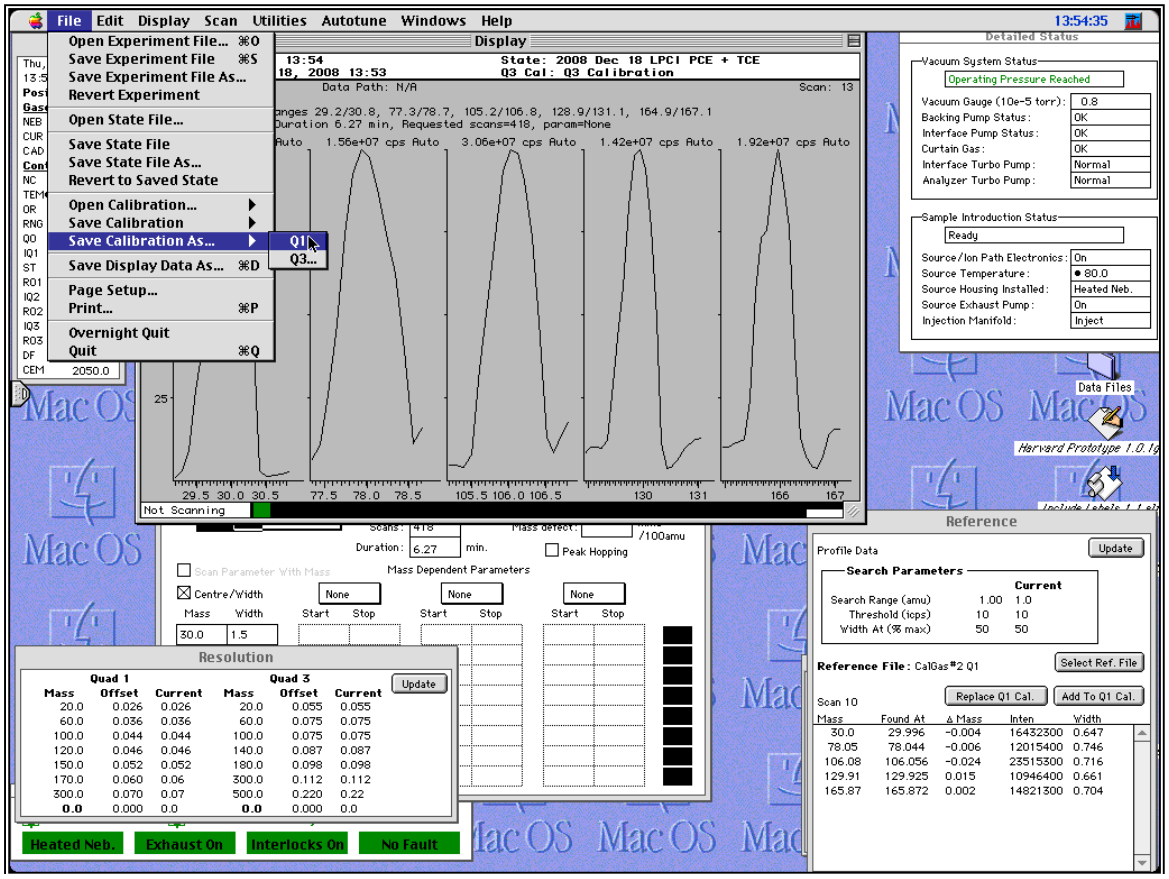

Figure 7.4.7 Replacing the Q1 Calibration

16) **Do not save** to the desktop. Instead, select US EPA 1or 2/Instrument/Calibration (Figure 7.4.8).

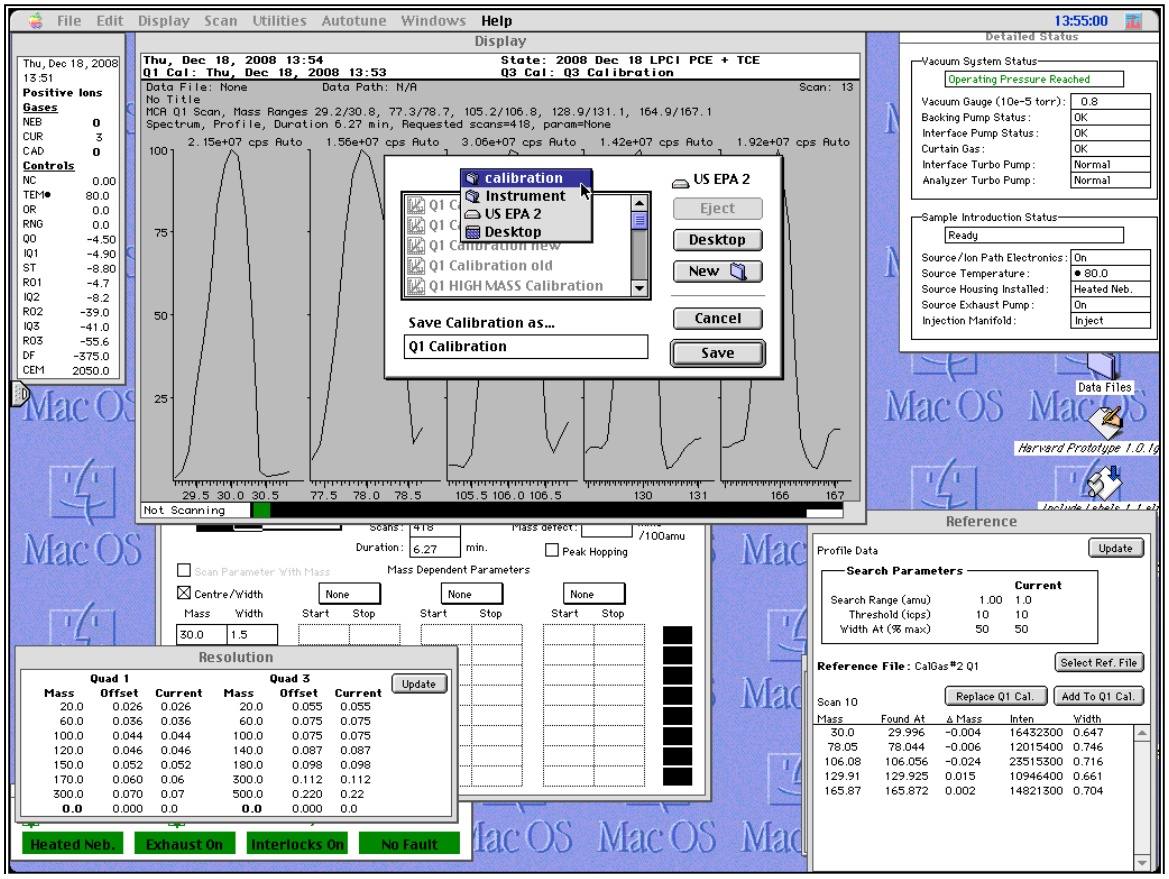

Figure 7.4.8 Selecting the Correct Folder for Q1 Calibration

17) Select [REPLACE] (Figure 7.4.9) to replace the current file.

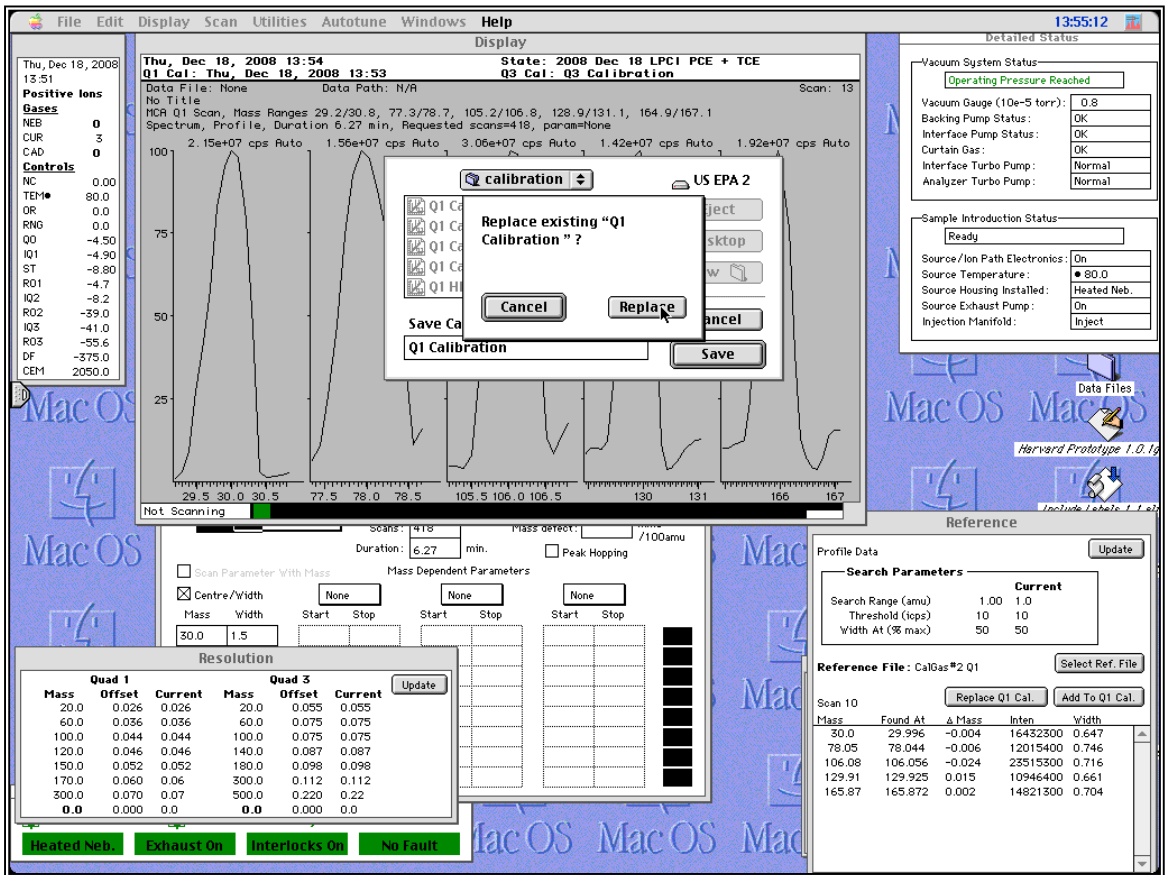

Figure 7.4.9 Replacing the Previous Q1 Calibration

Note: the upper left portion of the date in the display now indicates (Q1 Calibration). This calibration file is not part of the State File, and errors with the instrument calibration files cannot be corrected by loading a previous State File.

18) If peak widths are greater than 0.80, the "offset" values in the Resolution window must be adjusted.
19) Menu bar → [SCAN] [FINISH] [SCAN] [MCA] [SCAN] [START].
20) Adjust individual masses by clicking in the "Offset" column and making adjustments. Make adjustments by typing in the changes in small increments. Increasing the offset value narrows the peak width, while a decrease in the offset value broadens the peak width.
21) Click the [UPDATE] button in the Resolution screen after each incremental change. Proceed until all peak widths are within the 06.0 to 0.80 range. Changes in one range affect the other ranges. This is an iterative process. This process also tends to change the value of the mass assignment.
22) Menu bar → [FILE] [PRINT] [PRINT]. Click on the Reference screen, Menu bar → [FILE] [PRINT] [PRINT]. **Note: this printout is the only documentation of having met tuning**

criteria. The SCIEX software does not save this information.

23) Menu bar → [SCAN] [FINISH] [SCAN] [MCA] [SCAN] [START].
24) Now repeat the process for Q3. The procedure is the same, except on another quadrupole.
25) Return the CAD setting to its original setting (usually about 3 or 4).
26) Menu bar → [FILE], [OPEN EXPERIMENT FILE].
27) Select [LPCI Q3 READY] [OPEN]. This selects an experiment that scans selected mass ranges, with a step interval of 0.1. \
28) In the Reference window, click on the [Select Ref File] [LPCI MCAL Q3].
29) Click [PEEK] to verify required masses. Click [DONE] [OPEN].
30) Menu bar → [SCAN] [MCA] [START]. The instrument will start scanning, presenting a scan of the selected regions.
31) If the Δ masses are less than 0.15 amu and peak widths are between 0.60 and 0.80 amu, the calibration is acceptable. If not, go to step 11 and follow through step 21, but for Q3.
32) From step 21, allow the acquisition of 10 to 20 scans. Menu bar → [SCAN] [FINISH] [SCAN] [MCA].
33) Menu bar → [FILE] [SAVE STATE FILE].
34) Menu bar → [FILE] [PRINT] [PRINT]. Click on the Reference screen, Menu bar → [FILE] [PRINT] [PRINT]. This will make hard copies of all the current calibration information, peak widths, and mass assignments.

7.5 Calibration of Sample Air Flow and Standard Gas Flow

Before calibrating the TAGA on the first day of the week for any specific job, the mass flow controllers used to deliver standard and sample air flow to the instrument must be calibrated. There are forms for recording the results of this calibration at the end of the TAGA Log Book.

1) Disconnect the hose from the bottom of the sample introduction splitter, so the SAF is disconnected from the TAGA inlet. Connect that hose to the top connection on the Dwyer rotometer, which is calibrated in cubic feet per hour (CFH). On the TAGA computer, open the Excel spreadsheet titled Calibration 2 in the Calculation Aids folder. Note that for a SAF of 1500 mL/sec, the equivalent CFH will be about 191.
2) If the SAF is not already on, turn it on by pressing [ON], [3] on the MKS box, and let the flow stabilize.
3) Make sure the setting for channel 3 is 1500 (see Appendix D)
4) Adjust the span for channel 3 (Refer to the TAGA manual) until the Dwyer reads approximately 191 at the top of the ball. Record the flow and the span setting on the calibration log. The SAF is now calibrated.
5) Disconnect the Dwyer and replace the hose onto the TAGA inlet.
6) Use the Gillibrator calibration bubble meter (stored in the metal 'suitcase' in the mobile laboratory) to calibrate the mass flow controller (usually channel 1) to be used for calibrating the TAGA.
7) Turn on the standard gas cylinder, and make sure 20 to 40 psig is sent to the appropriate mass flow controller.
8) Manually start the standard flowing, at the MKS box press [ON], [1], and set the flow to a mid-level flow, such as 60 mL/min (see Appendix D).
9) Take an average of ten readings of the flow on the Gillibrator. If the flow is more than 2% off, change the span for channel 1 to adjust the flow, just as you did for channel 3. It may

take several iterations to get the flow within 2%.

10) Once the span is adjusted for the mid-range flow, take an average of 10 readings each at 90, 30 and 10 mL/min, and verify that the maximum error is under 10%. Record all of the readings, along with the channel 1 span, in the TAGA calibration log.
11) If necessary, repeat the procedure for channel 2.

7.6 Target Compound Calibration

TAGA calibration is essentially done using the Method of Standard Addition. Using ambient air as the matrix, the concentrations of targeted compounds are increased by known amounts (five concentrations and a zero point). A linear regression line is calculated through all six points (five steps plus 'zero'). The slope calculated by the linear regression, not forced through zero, is used to calculate ambient concentrations, with the assumed intercept of zero. This procedure is valid so long as the calibration is linear throughout the range of measurement.

The calibration is performed as near to the monitoring site as practicable. Since ambient air is used in the calibration, based on the analyst's judgment, if the background level of targeted compounds is unacceptable the mobile laboratory should be moved to a location expected to be representative of the general background ambient air, but with little or no local sources of target compounds. The ambient air is then used as the 'zero' in the calibration, and the individual calibration concentrations.

The procedure described in this section assumes that the standard concentration used for calibration is approximately 20 ppmv for each compound in a balance of nitrogen. Other methods for providing calibration standards are often used, and usually make use of the Harvard Syringe Drive (Appendix E). The differences among the methods lie in the procedures used for generating and introducing the standards.

1) Open the Excel program by icon on Desktop or using the Apple icon at the menu bar.
2) It is assumed that all required methods, experiments, MRM table, concentration tables, etc. have been created prior to calibration. If not, see table of contents for those sections specifically designed to address their creations. The example to follow will use PCE and TCE as the target compounds.

3) Menu bar → Apple icon → [TAGA-EXPRESS] (Figure 7.6.1). **Note:** as soon as the software enters this routine, the state file stored in the instrument is cleared, and the curtain and collision gases are turned off. If the Detailed Status pane is open, notice as the pressure drops rapidly.

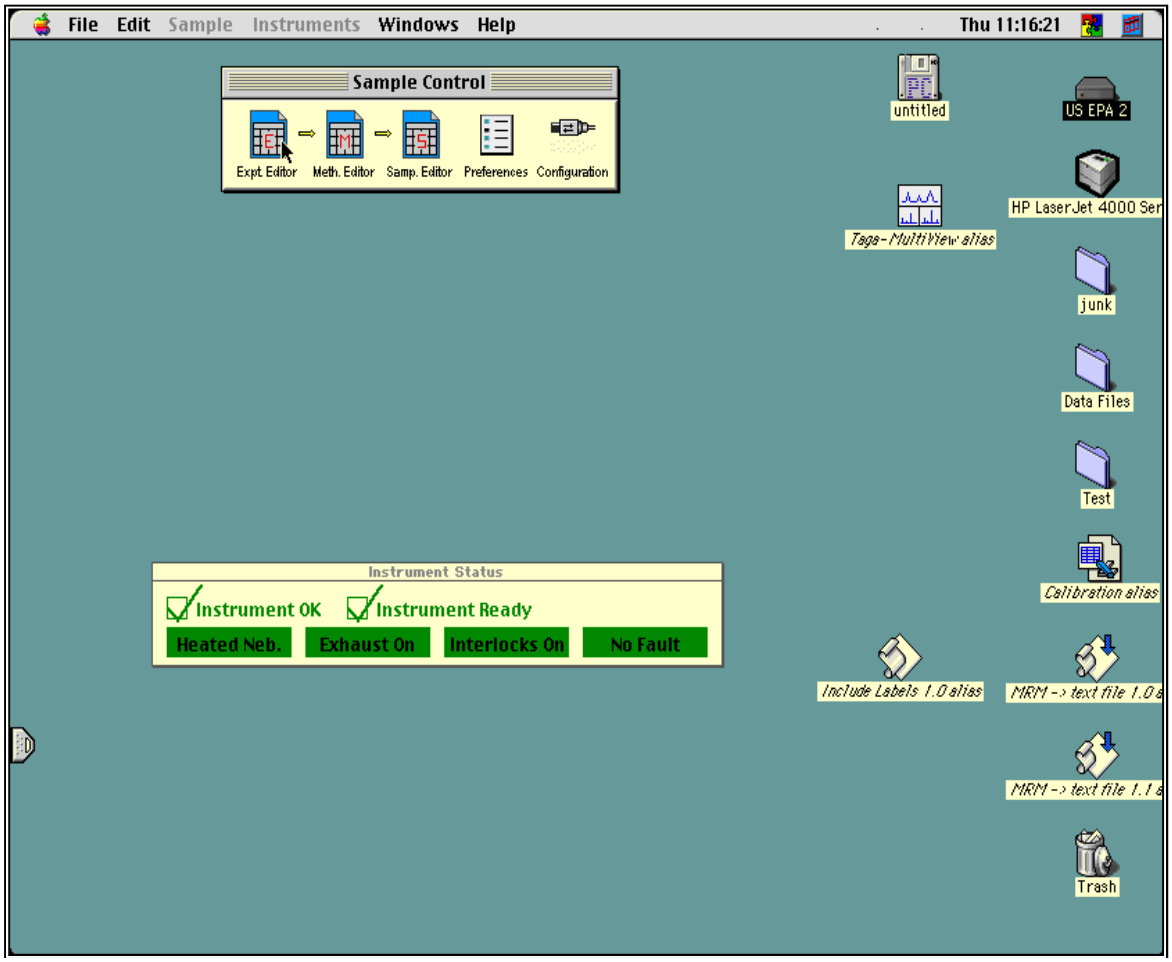

Figure 7.6.1 Initial Sample Control Screen

4) In the Sample Control screen, double click on the Meth. Editor icon to open dialog box (Figure 7.6.2).

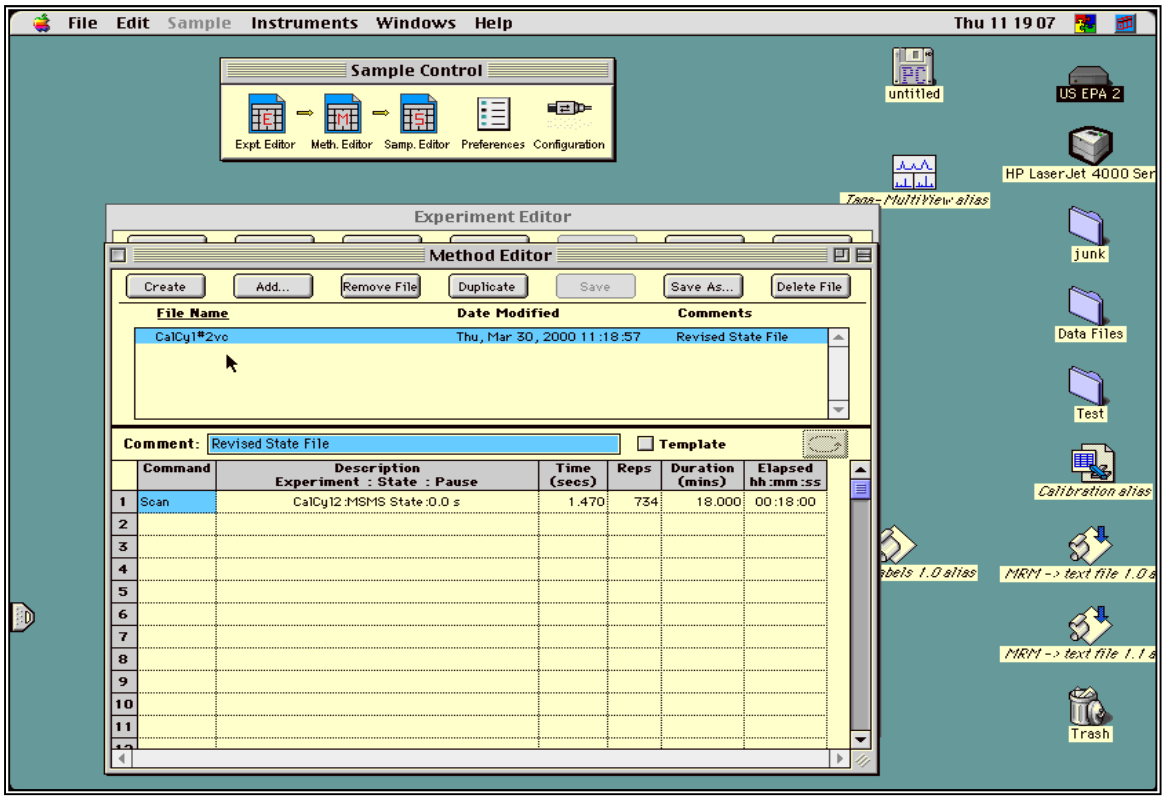

Figure 7.6.2 Method Editor

5) Click the [ADD]. This brings up the list of available Methods.
6) Select the appropriate calibration method, for example: select "PCE/TCE Calibration". Click [ADD] [DONE].
7) Double click the information in the Description column. This opens an edit box (Figure 7.6.3).
8) If any changes are needed, use the selection buttons in the pane to change the selections.
9) Ensure that the correct Experiment has been selected.
10) Using the drop down dialog box, ensure that the State File saved after tuning was completed has been selected.
11) Ensure that both Q1 and Q3 Calibration files selected are the same as saved during tuning.
12) For maximum sensitivity, be sure that the Threshold is set at 0.1×10^1 counts per second (the SCIEX software will not accept an exponent of zero).

13) Click [OK]. Click [SAVE] button. This will activate a device loading process which will take about a minute.

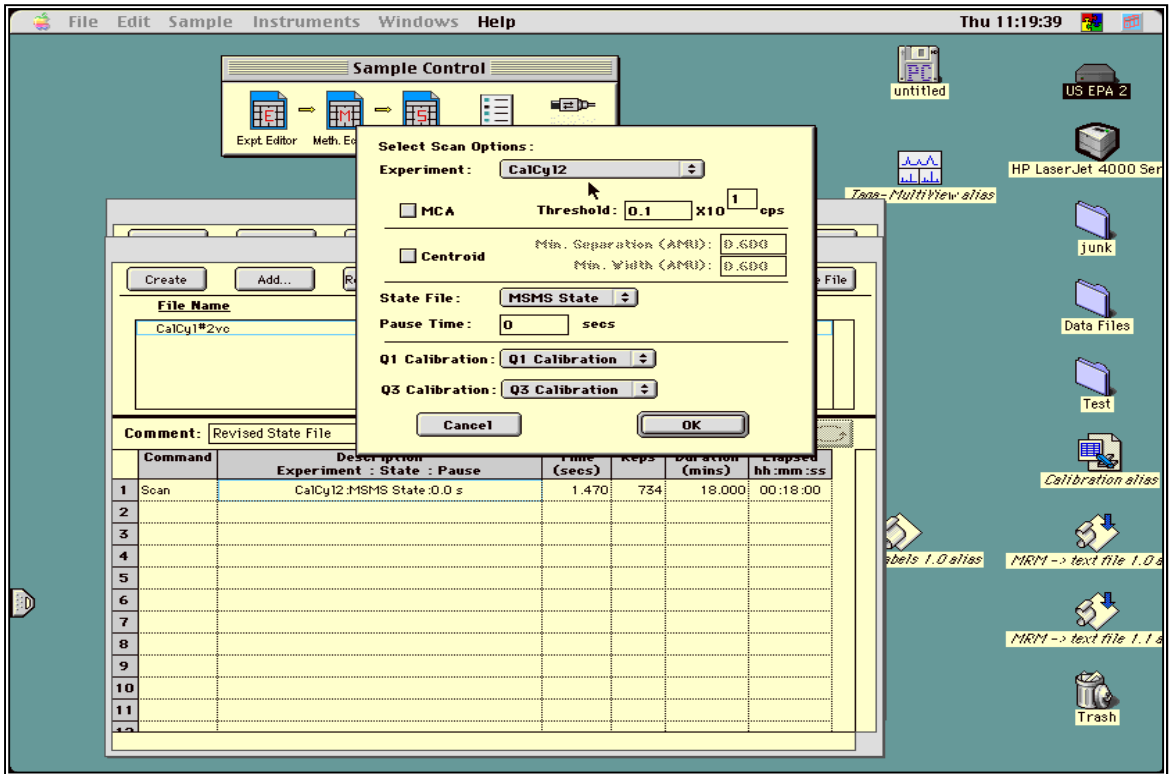

Figure 7.6.3 Changing Selected State and Experiment in Method Editor

14) When completed, go to the menu bar → [FILE] [PRINT] [PRINT]. This will document the State and Experiment files. Verify that the current daily State file is what is in use.
15) In the Method Editor screen, click [ADD]. This brings up the list of available methods.
16) Select the appropriate monitoring method, for example: select "PCE/TCE Monitoring". Click [ADD] [DONE].
17) Double click the information in the Description column. This brings up an additional edit box (Figure 7.6.3).
18) Repeat steps 9 to14. Close the Method Editor.

19) Click on the Acquire Sample box. (Figure 7.6.4)

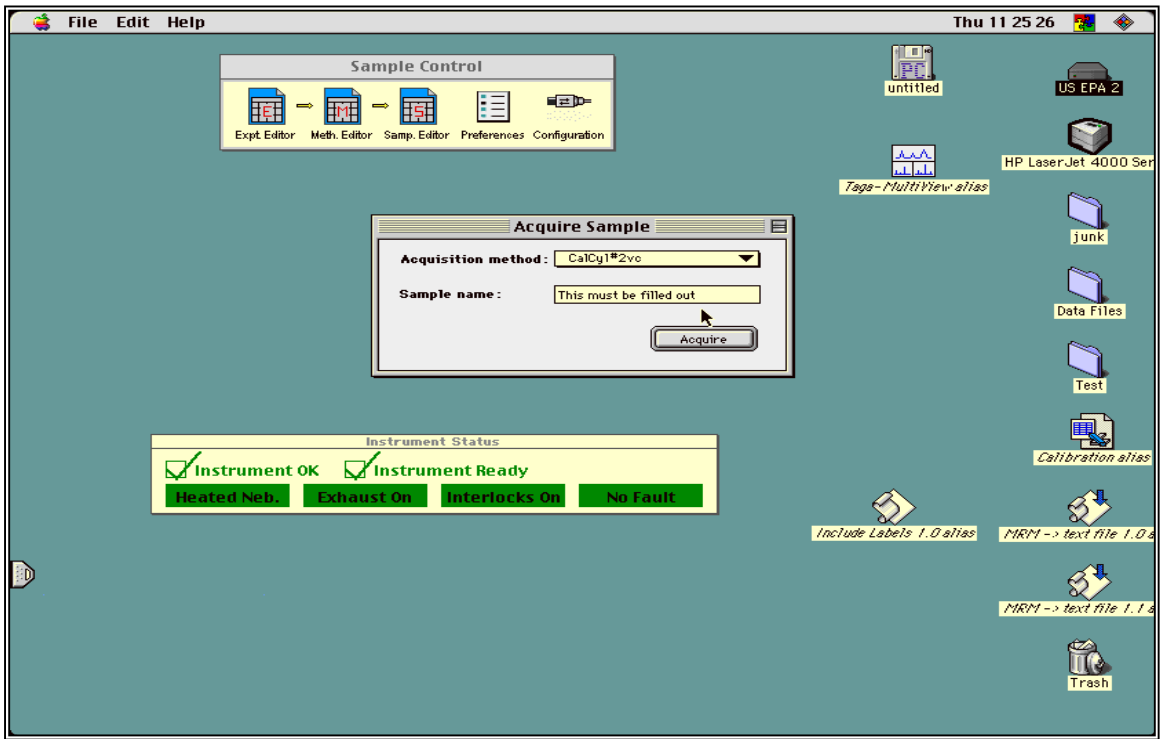

Figure 7.6.4 Initial TAGA EXPRESS Pane

20) Using the drop box select the acquisition method for calibration loaded from the Method Editor. Select PCE/TCE Calibration. **Note:** that if you created monitoring and calibration methods with new names, these files will not be available until you exit TAGA EXPRESS and re-load TAGA EXPRESS. TAGA EXPRESS loads a list of available methods when it is first loaded.
21) At the keyboard, depress the Caps Lock key.
22) In "Sample Name:' type in BOD CALIBRATION or other appropriate name. (BOD = Beginning of Day)

23) At the menu bar → [EDIT] [PREFERENCES]

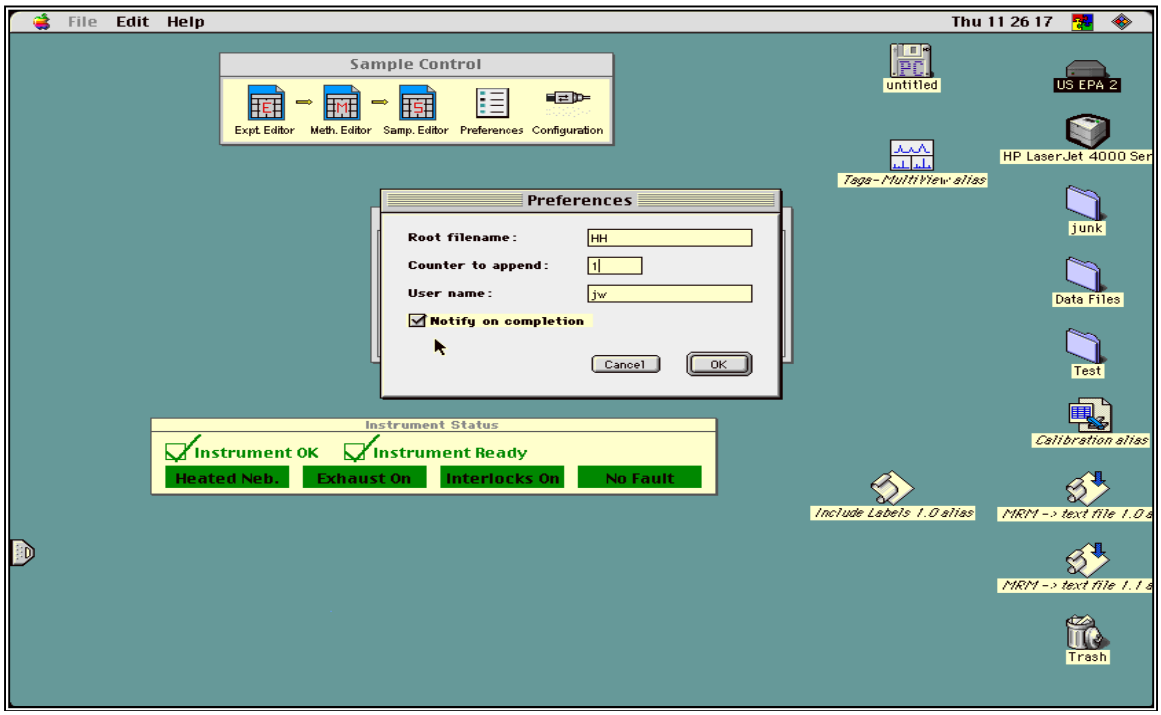

Figure 7.6.5 TAGA EXPRESS Preferences

24) Enter the appropriate 'root file name' and 'counter to append', as shown in Figure 7.6.5. The 'root file name' is the basic file name used in the upcoming run or series of runs, and the 'counter to append' is the number added to the end of the file name. This number is incremented after each run. If the 'root file name' is HH, and the 'counter to append' is 1, the resulting file name will be HH001. After that run is completed, the next run under TAGA EXPRESS will be named HH002 automatically.
25) Check the 'Notify on Completion' box, or TAGA EXPRESS will not let you know when the run is completed.
26) Click [OK]. This accepts the values and returns you to the previous screen.
27) Enter file information as appropriate. **Something must be entered in the file information area, or the software will not allow you to continue.**
28) At the instrument inlet area, connect the Teflon tubing to the glass splitter. At the calibration gas cylinder, open the valve.
29) At the computer, click [ACQUIRE]. A confirmation pane will appear, asking if you want to continue. Review the file name, and if correct, continue. (If not correct, select [CANCEL], and return to [EDIT], [PREFERENCES] to make the corrections).
30) MULTIVIEW application will open and the real time total ion chromatogram (TIC) will be displayed.
31) Adjust the TIC display so that the Detailed Status and the Status Window screens are visible. This will monitor the vacuum status in the Detailed Status and the minutes into the acquisition

in the Status Window.

32) The calibration run will proceed automatically, with the TIC being displayed. The horizontal time scale is automatically set to the total run time (Figure 7.6.6). Note that the scaling of the vertical (intensity) axis is automatic.

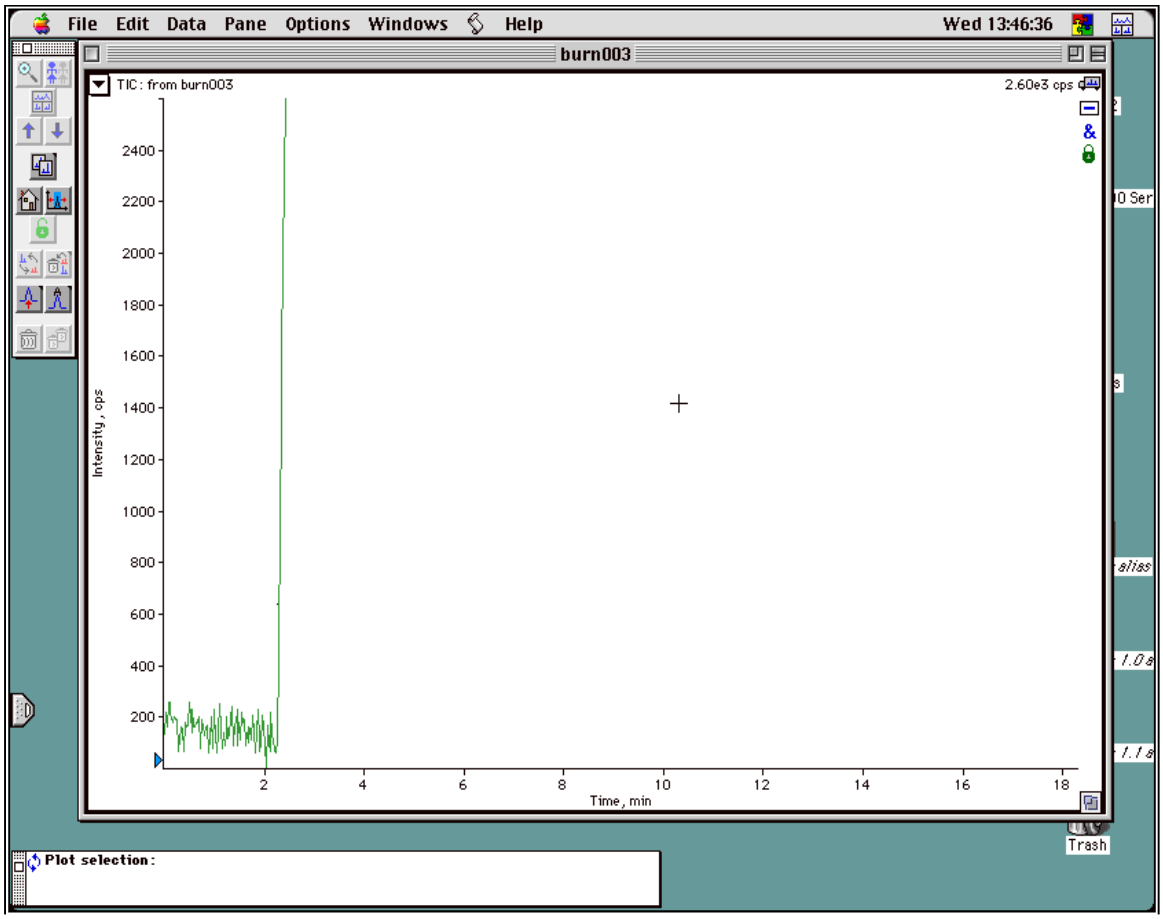

Figure 7.6.6 Start of Calibration Run

33) To monitor the progress of the calibration for one or more specific compounds, select [PANE], [EXTRACT IONS], [USE DIALOG] (Figure 7.6.7).

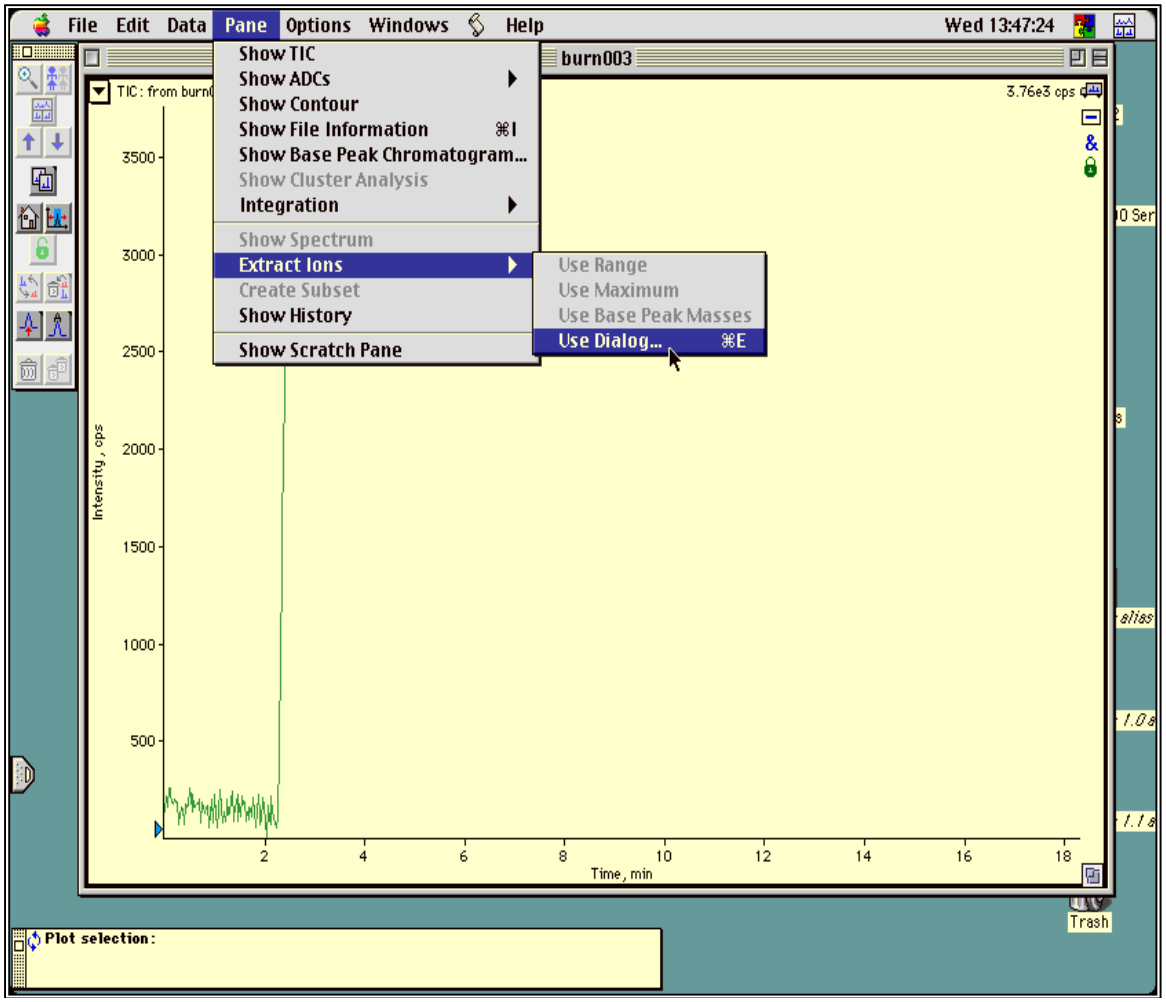

Figure 7.6.7 Preparation to Monitor Selected Ions

34) Select the ion pairs to monitor (Figure 7.6.8).

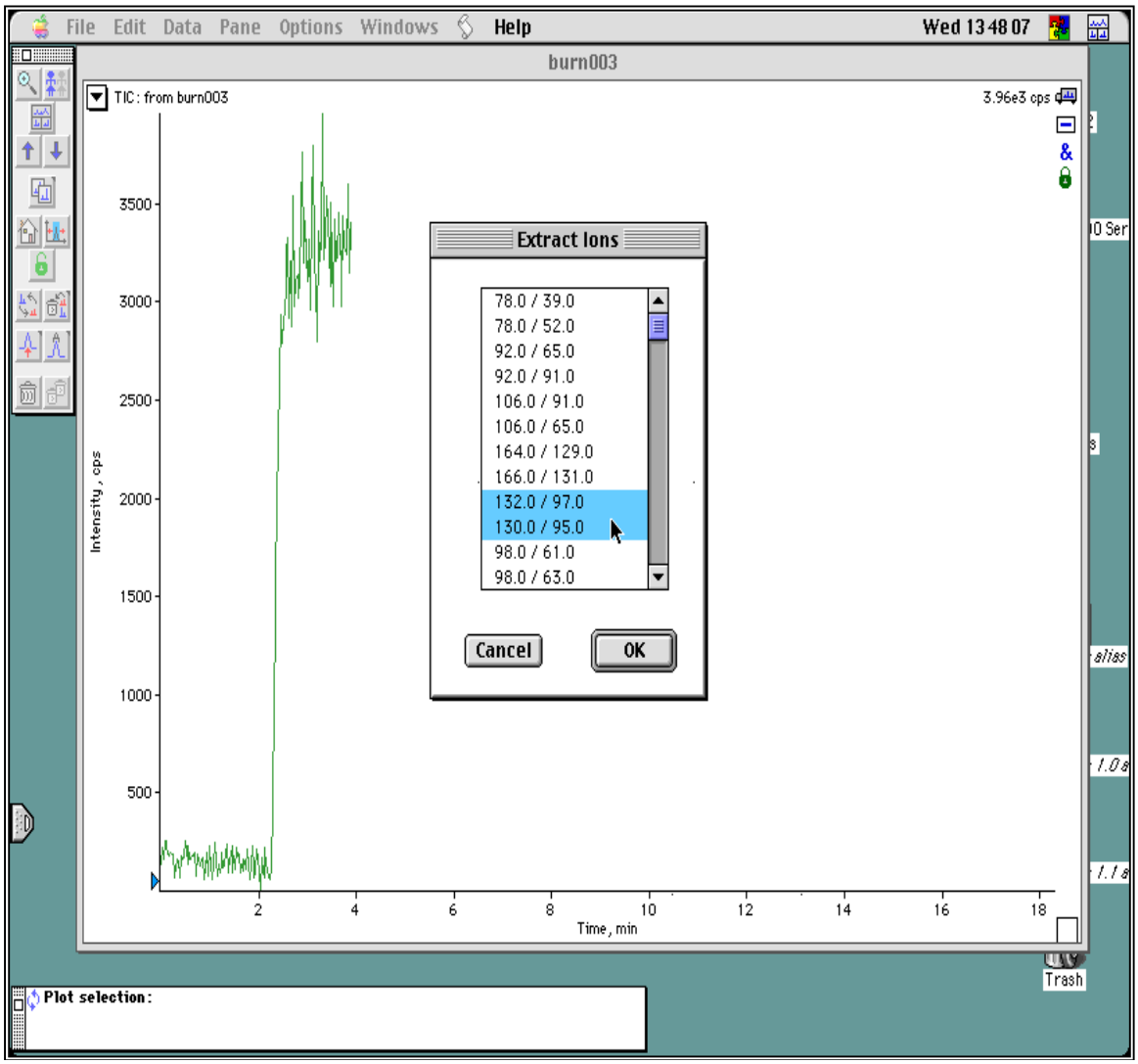

Figure 7.6.8 Ion Pair Selection

35) The selected ions will be displayed in a pane below the TIC pane (Figure 7.6.9). If more than one ion pair is selected, the pair displayed at the top of the pane will be displayed as a solid line, and the others will be displayed as dashed lines. To select another ion pair to be displayed as a solid line, click and hold on the selected ion pair. That will drop down a menu of available ion pairs. Move the pointer to the new selection and then release the mouse button to complete the selection.

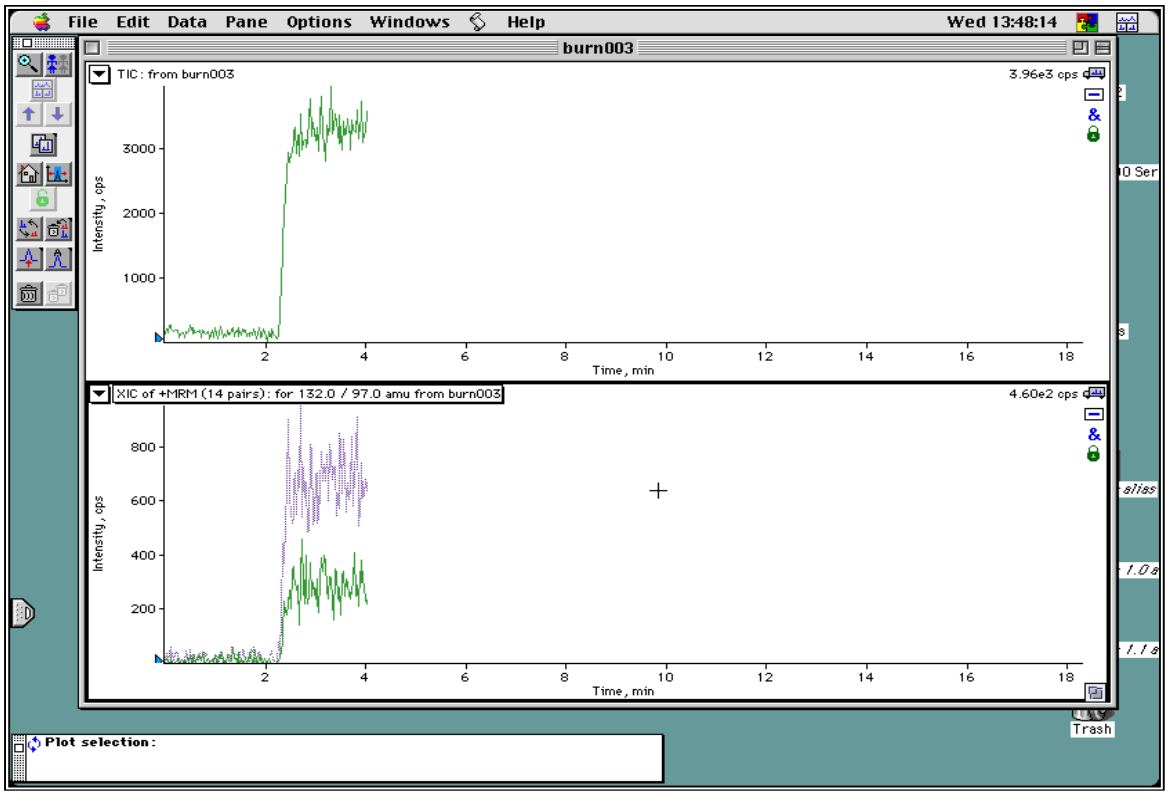

Figure 7.6.9 Display of Extracted Ion Chromatograms

36) Allow all the calibration levels to be acquired. This should take about 15 to 20 minutes.
37) To end the run early, click the furthest right hand side of the menu bar → TAGA Express.
38) The Acquire Sample box will appear. Go to the menu bar → [FILE] [ABORT] [OK].
39) The MULTIVIEW screen will be visible, with the TIC of the just-completed calibration run active.
40) Close valve at the gas standard cylinder.

41) Hold the shift key down, then move the cursor to the center of each calibration level, clicking once in each level, including zero, from lowest to highest (Figure 7.6.10). **It is very important that the levels are selected in the same incremental order as present in the concentration tables; otherwise, the software will not identify the levels correctly.**
42) At the menu bar, click on the Scroll icon → [CREATE CALIBRATION].

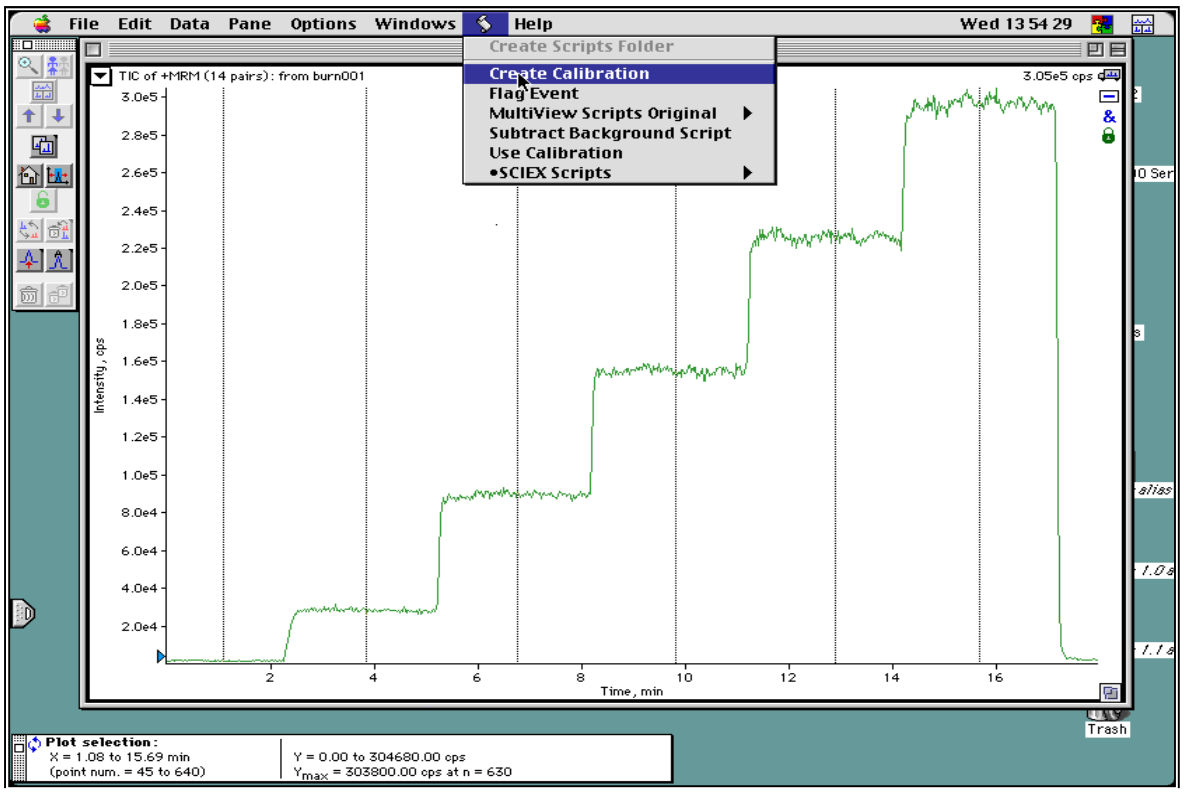

Figure 7.6.10 Selection of Calibration Levels

43) The available compounds will be displayed (Figure 7.6.11). If required compound is not displayed, then it is not included in the MRM Table. The appropriate MRM Table must be loaded and the compound added to the MRM Table. The procedure for these actions is found in section 7.9

44) Select the compound. This loads the concentrations for the calibration levels (Figure 7.6.11). **Verify that the concentrations listed on the screen are consistent with the standard cylinder being used and the flow rates selected for the calibration. Be sure the concentration table has been updated. If the highest standard flow rate is 90 mL/min and the SAF is set to 1500 mL/sec, the highest concentration displayed in ppbv should be numerically the same as the concentration in ppmv in the cylinder.**

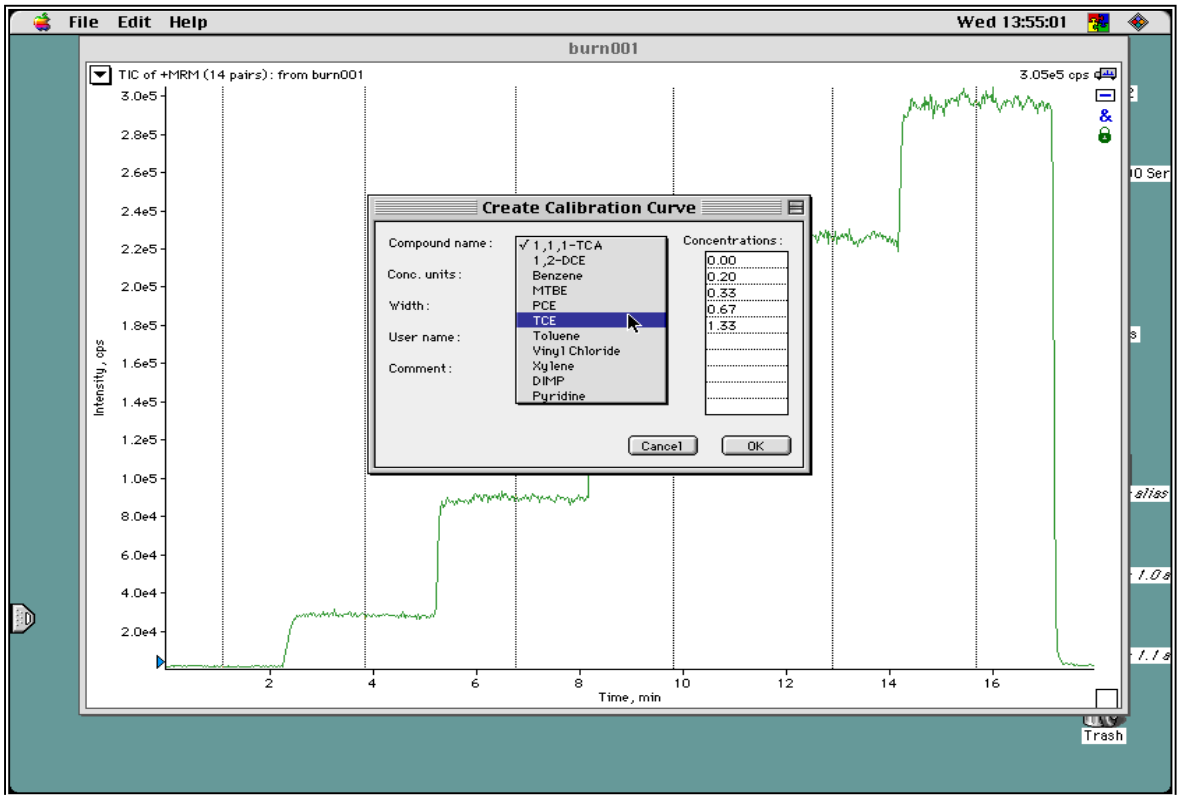

Figure 7.6.11 List of Available Compounds

45) Select an appropriate calibration window for the calibration run and the project. The 'width' in the example is 0.5 minute. This results in averaging the signal 0.5 minutes on each side of the selected point for a total averaging width of 1.0 minutes. A time other than 0.5 minutes may be selected. However, the time must include at least 30 complete sequences. If the time for one sequence exceeds 2.0 seconds, a 'width' of greater than 0.5 minutes must be selected.

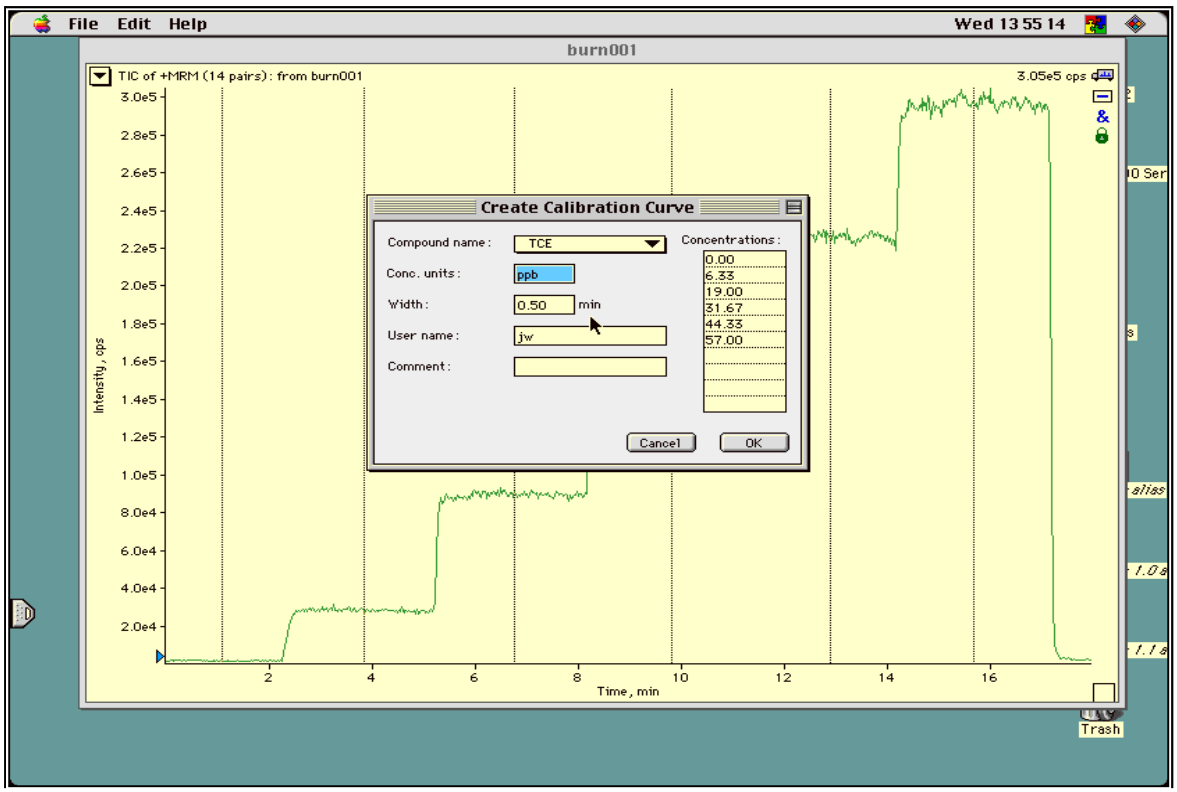

Figure 7.6.12 Calibration Screen for Selected Compound

46) If needed, change the 'User Name:' and 'Conc. Units:'. Click [OK].

47) The software will process the calibration, and then display in EXCEL the calibration curve, correlation coefficients, and the average response and concentration for each level (Figure 7.6.13).

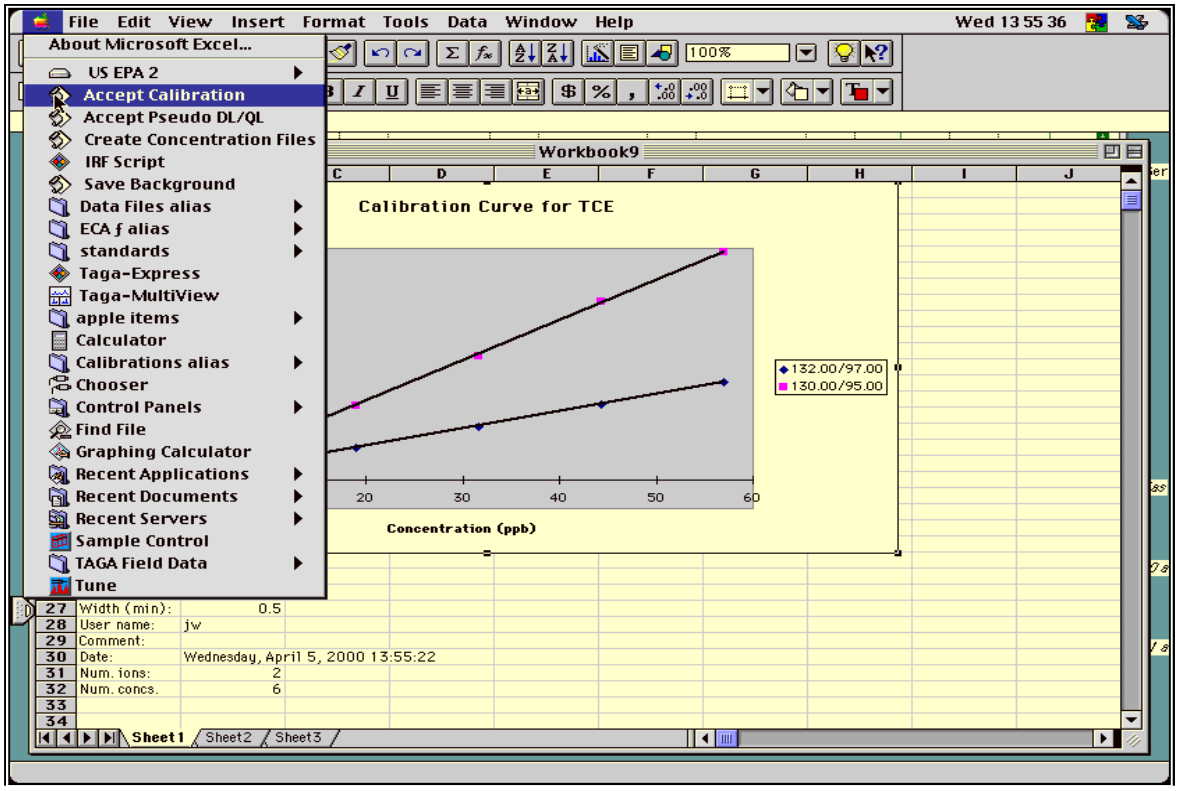

Figure 7.6.13 Accept Calibration

48) At the menu bar, click on the Apple icon [ACCEPT CALIBRATION]. This loads the Excel file into the appropriate directory for use by the software (EPA1/System Folder/Preferences/ECAf/Calibration).
49) At the menu bar, [FILE] [PAGE SETUP]. In the Scaling section, check for "Fit to 1 Page" [PRINT] [PRINT].
50) **Note: the software does not identify which compounds have or have not been calibrated and/or 'Accepted'. It is the responsibility of the analyst to keep track of this. The hardcopy printout may assist in this tracking.** *If these steps are inadvertently skipped, a previously existing calibration will be used to quantify acquisitions and that fact may not be immediately obvious. If in doubt, look at the file dates for the spreadsheets in* US EPA(1 or 2)/System Folder/ Preferences/ ECAf/Calibration.
51) Close the worksheet. Worksheet is not saved.

52) After the first calibration is accepted, the TIC displays the window used for averaging the ion count response for each level (Figure 7.6.14). Verify that range selected was correct.

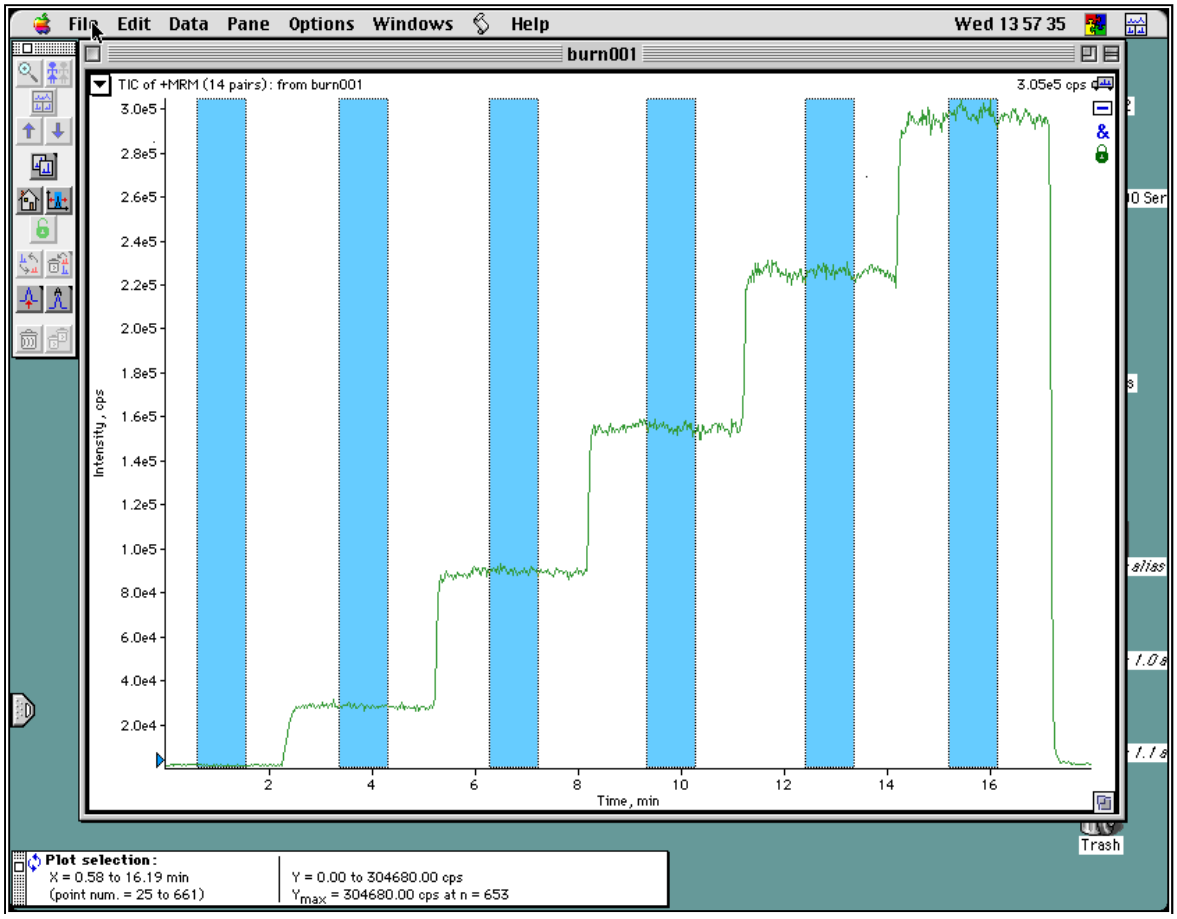

Figure 7.6.14 Averaging Range for Each Level

53) Once all compound calibrations have been completed and accepted, then calculate the detection limits. At the menu bar, click on the script icon (Figure 7.6.14), select [USE CALIBRATION].

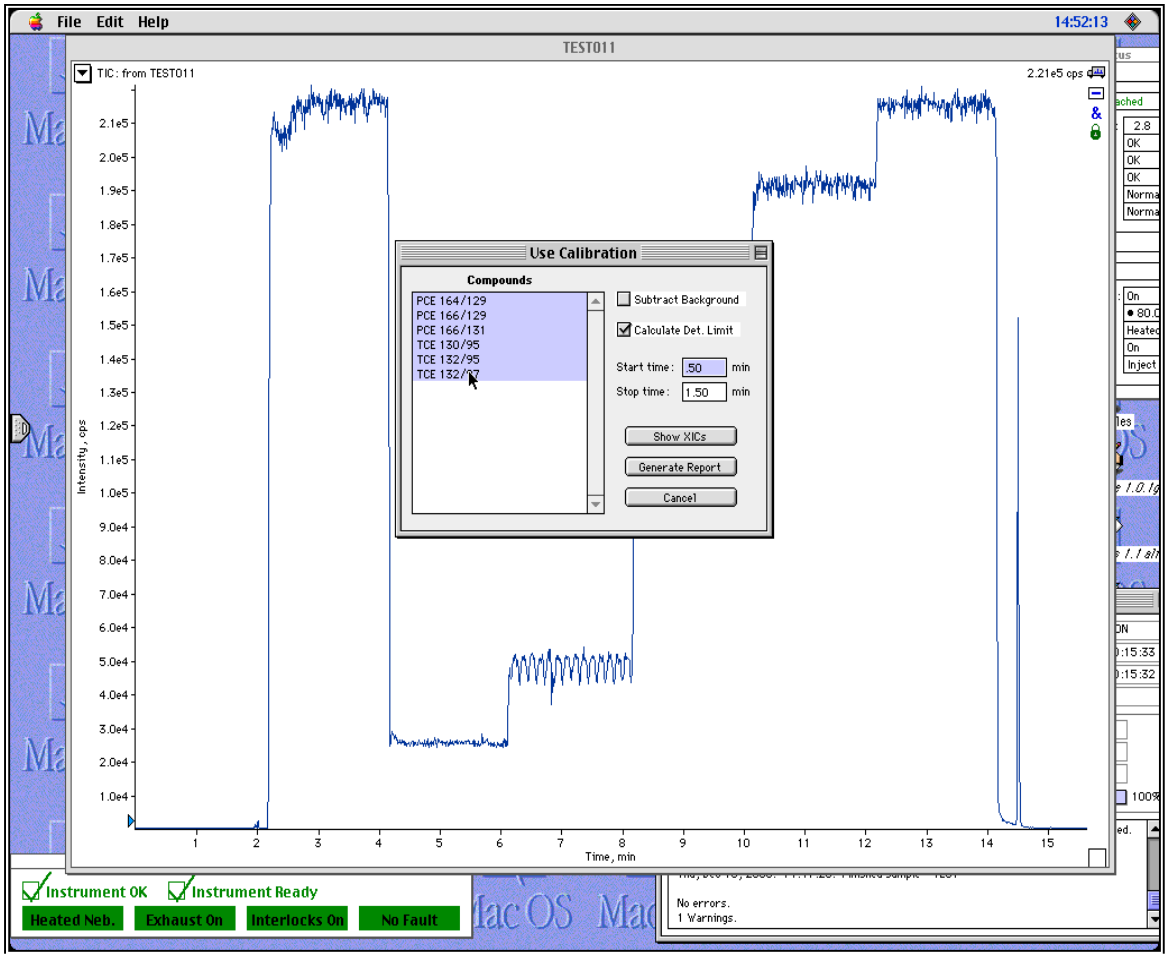

Figure 7.6.15 Selecting for Detection Limits

54) In the 'Use Calibration' window (Figure 7.6.15), select the ion pairs to be included in the detection limit calculation.
55) Click the 'Calculate Detection Limit' box.
56) Type in the 'Start Time' and the 'Stop Time' of the baseline period ('0' point) during which the detection limit is to be calculated.
57) Review the selections, select [GENERATE REPORT].

58) The software will process the data and calculate detection limit (DL) and quantitation limit (QL) for each of the compounds. An Excel worksheet will open and display the report (Figure 7.6.16).

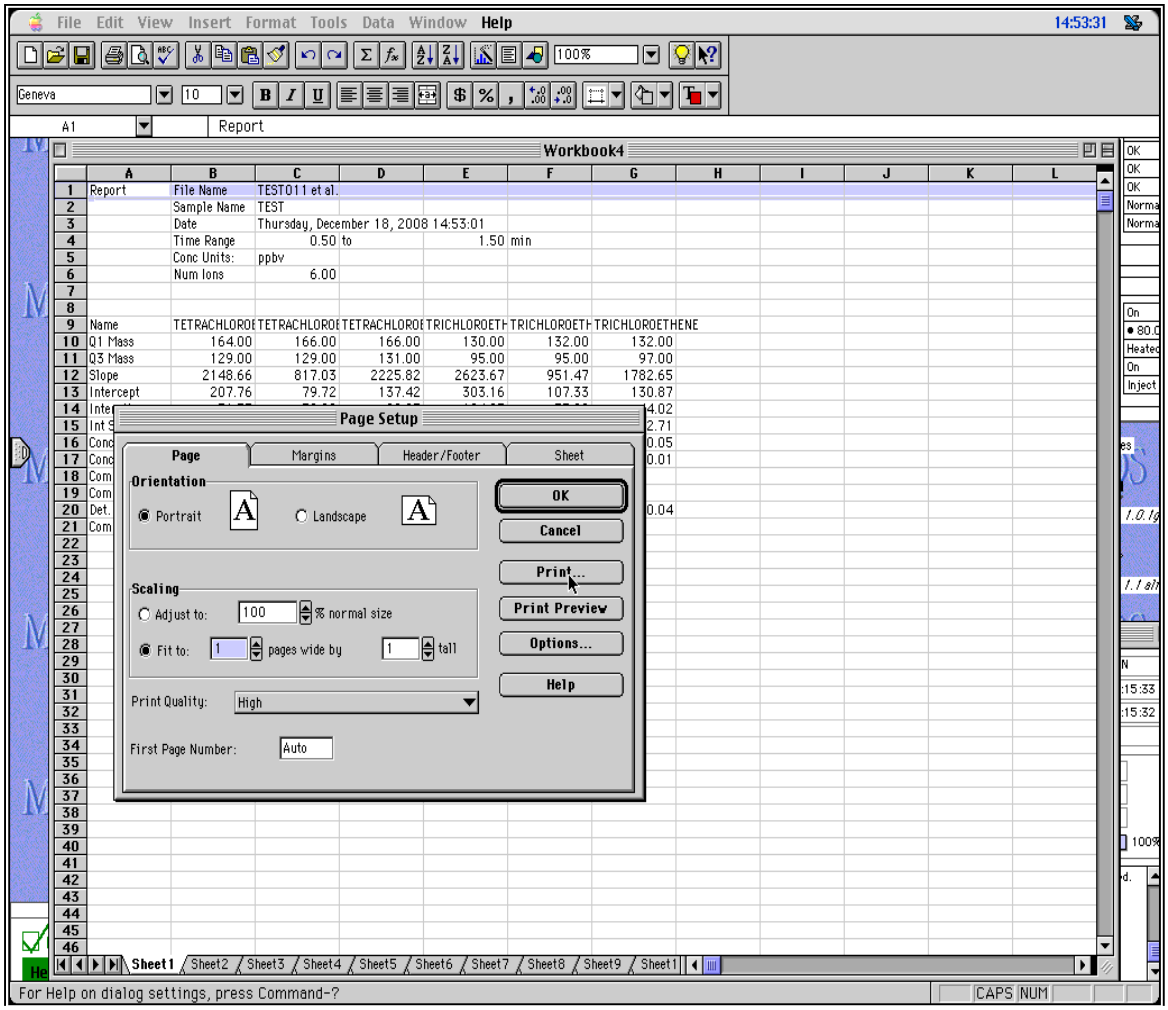

Figure 7.6.16 Printing the Detection and Quantitation Limits

59) At the menu bar, [FILE] [PAGE SETUP] [LANSCAPE] ['Fit to 1 page wide by 1 page tall] [PRINT] [PRINT]
60) Close the worksheet. Worksheet is not saved.

61) The acquired analysis will be displayed in two panes (Figure 7.6.17). Click on the bottom pane and then click on the 'Garbage can' icon at the bottom of the left hand tool box. This will delete the bottom pane.

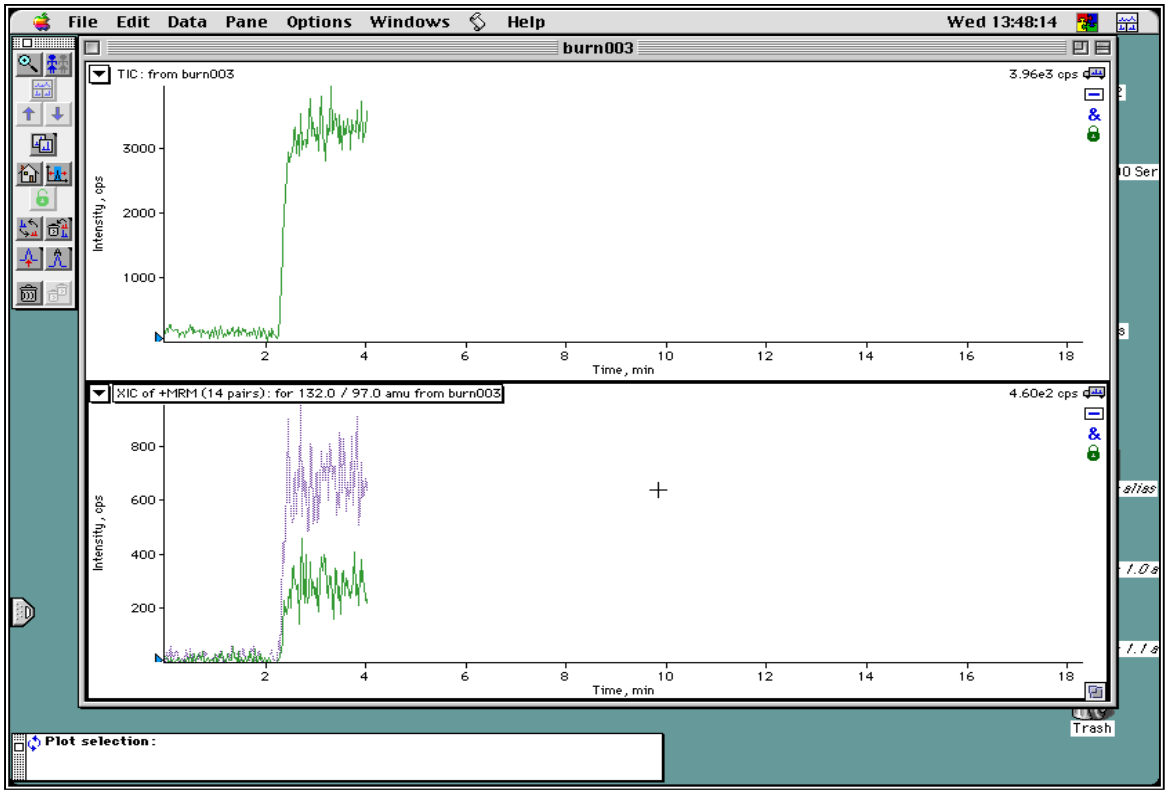

Figure 7.6.17 Removing panes from the TIC display

62) At the menu bar, [FILE] [PRINT] [PRINT].
63) Staple all printouts together and place in calibration folder.
64) Close the file. Calibration process completed.

7.7 Acquisitions

1) After completion of any acquisition, computer will return to the initial TAGA EXPRESS display (Figure 7.7.1).

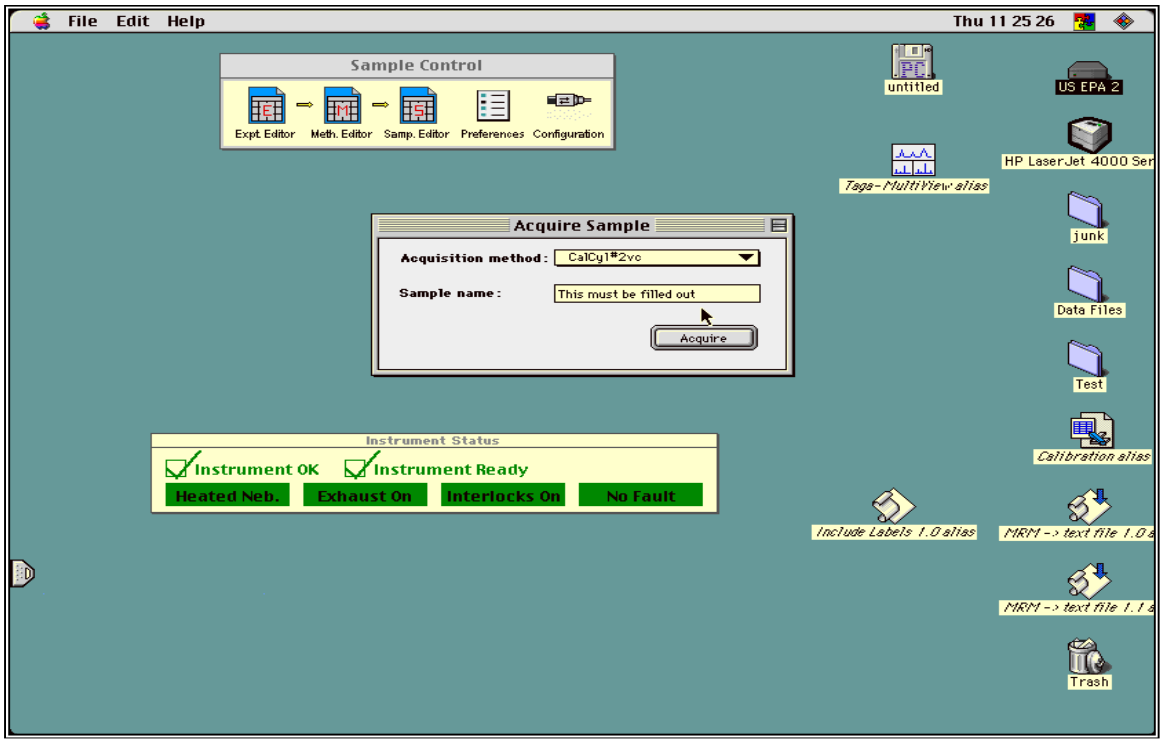

Figure 7.7.1 Initial TAGA EXPRESS Pane

2) Using the drop box select the acquisition method for monitoring loaded from the Method Editor. Select PCE/TCE Monitoring.
3) Ensure Cap lock is toggled "On".
4) The file naming system should have been entered before the calibration acquisition. If not or change is required, go to the menu bar, [EDIT] [PREFERENCES]. Make necessary corrections to 'Root file name' and 'Counter to append'.
5) Enter the appropriate information in 'Sample Name'.
6) If the monitoring events call for the use of the 200 to 300 foot Teflon hose, the next acquisition will be "Transport Efficiency".

7.7.1 Transport Efficiency

Transport efficiency is performed first, to ensure that the Teflon hose is leak free. Secondly, to determine the percentage of a target compound's known concentration that will reach the MS/MS under current operating conditions.

1) At 'Sample Name:' type in "BOD TRANSPORT" (BOD = Beginning of Day).
2) An apparatus to facilitate the transport efficiency acquisition is pictured in Figure 7.7.2. It is comprised of a Swagelok® three-port valve, a glass splitter, and three varying lengths of 1/8-inch Teflon tubing with suitable Swagelok® fittings at each end.

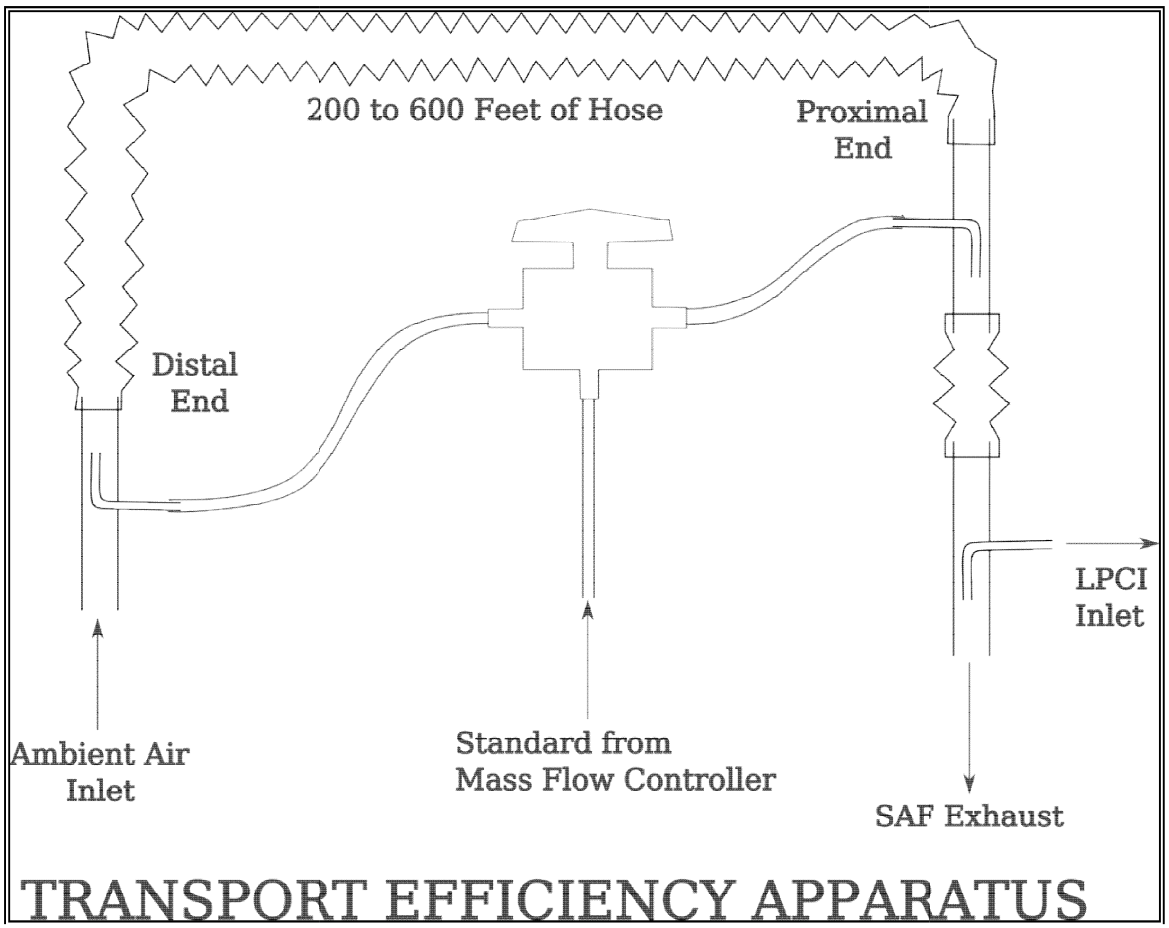

Figure 7.7.2 Layout of Transport Efficiency Apparatus

3) Connect the apparatus as shown in Figure 7.7.2 above.
4) Switch the valve to send the gas flow to the proximal end of the sampling hose.
5) Open valve at the gas standard cylinder.

6) At the MKS box, set the flow to 30 mL/min. See Appendix C for MKS instructions.
7) At the MKS box, [ON] [1].
8) At the Acquire Sample dialog box, click on [ACQUIRE]. A confirmation pane will appear, asking if you want to continue. Review the file name, and if correct, continue. (If not correct, select [CANCEL], and return to [EDIT], [PREFERENCES] to make the corrections).
9) MULTIVIEW application will open and the real time TIC will be displayed.
10) Adjust the TIC display so that the Detailed Status and the Status Window screens are visible. This will monitor the vacuum status in the Detailed Status and the minutes into the acquisition in the Status Window.
11) Wait for the signal intensity to stabilize.
12) Once the signal stabilizes, at the menu bar, select the 'script' icon → [FLAG EVENT]. Press a letter key (i.e., flag), then [OK] to record the flag. Record the event associated with the flag on the operator's log sheet (Figure 7.7.3).

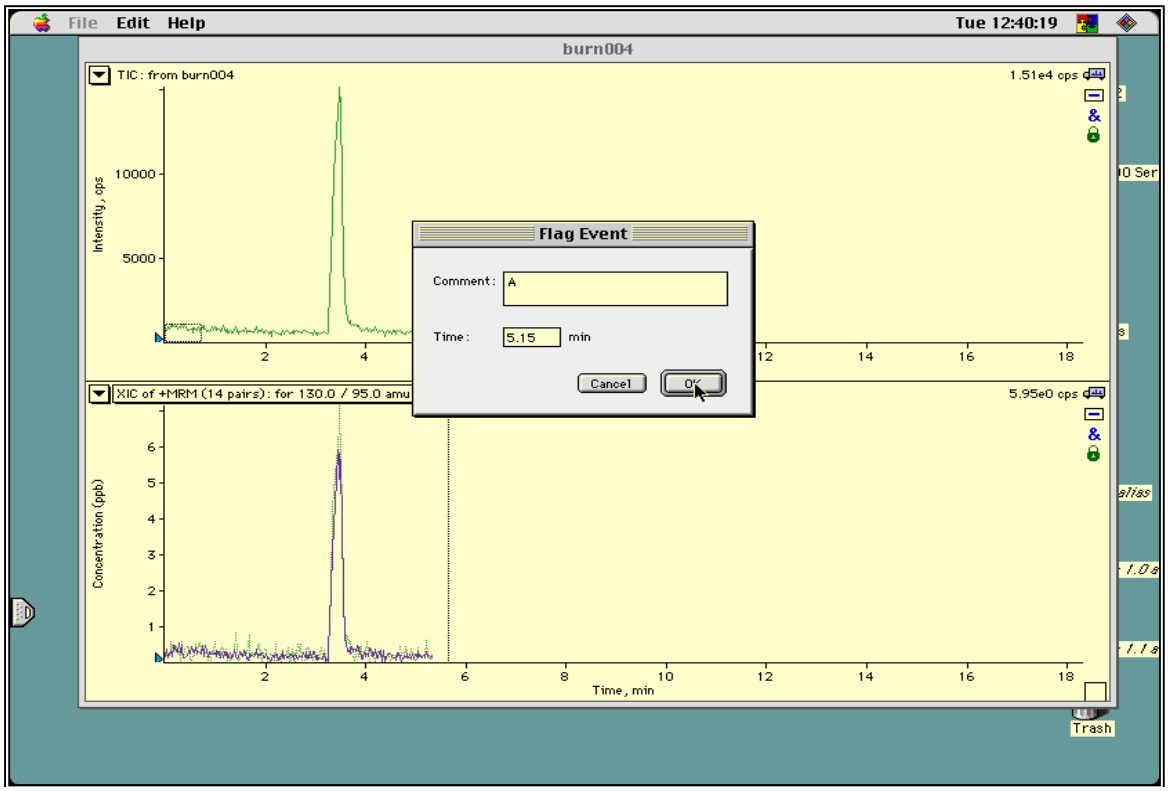

Figure 7.7.3 Setting Flag Events

13) Collect at least one minute of data and then set another flag and record the event associated with the flag on the operator's log sheet (Figure 7.7.4).
14) Turn the three-way valve, switching the gas standard flow from the proximal end to the distal end. Immediately flag the switch time. Menu bar → Scroll icon → [FLAGE EVENT] type in letter flag, [OK].
15) The signal will drop to nearly zero for a time and then it will start to rise. Immediately flag the rise.
16) Allow signal to reach its maximum and stabilize.
17) Collect at least one minute of data and then set another flag and record the event associated with the flag on the operator's log sheet.

TAGA Analysis Event Log

Date: March 28th 2005	Time: 15:20:34	Operator's Initials: TAA
Analysis Type: MRM	TAGA Filename: GT05055	Source Pressure (torr): 1.8
TAGA File Title: BOD Transport		

Flag	Time	Comments/Locations/Intersections/Landmarks/Sources
A	1:29	Start Proximal
B	2:29	End Proximal
C	2:47	Switch
D	4:29	Start Distal
E	5:30	End Distal
F		
G		
H		
I		
J		
K		

Figure 7.7.4 Transport Efficiency Event Log

18) Click on icon at upper right corner, select [TAGA EXPRESS].
19) At the menu bar, select [FILE] [ABORT]. This stops the run.
20) At the menu bar, [FILE] [PRINT] [PRINT]. This will print the chromatogram.
21) Close the file.
22) Staple all printouts together and place in folder.

23) Calculation for transport efficiency is the ratio of the signal observed when the standard is flowing into the distal end of the hose to the signal when the standard is flowing into the proximal end of the hose.
24) At the MKS box, [OFF] [1]. This shuts off gas standard flow.
25) Shut off valve at the gas standard cylinder.
26) Disassemble the Transport Efficiency apparatus and store appropriately.

7.7.2 Monitoring (Surveys)

1) Click on the Acquire Sample box (Figure 7.7.1).
2) Ensure appropriate monitoring method has been chosen.
3) In 'Sample Name:' type in appropriate name, for example; UNIT 001 SURVEY.
4) Check your file naming preferences if necessary; at the menu bar → [EDIT] [PREFERENCES], make necessary adjustments and click [OK].
5) In the 'Acquire Sample' box, click [ACQUIRE]. Confirm file name [OK].
6) MULTIVIEW application will open and the real time TIC will be displayed. Adjust the TIC display so that the Detailed Status and the Status Window screens are visible. This will monitor the vacuum status in the Detailed Status and the minutes into the acquisition in the Status Window.
7) To view the real time concentrations of targeted compounds, at the menu bar → click on the Script icon, [USE CALIBRATION]. The USE CALIBRATION pane will be displayed (Figure 7.7.5).

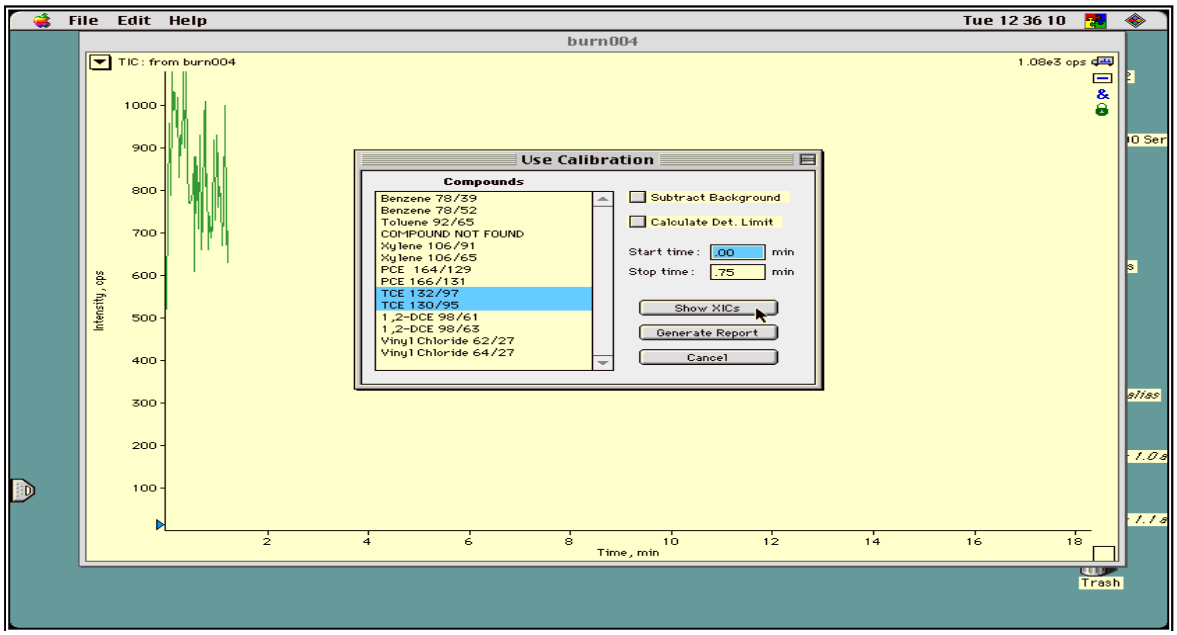

Figure 7.7.5 Selecting Quantitative Display with USE CALIBRATION

8) The ion pairs are listed in the same order as they appear in the Experiment, and the compound names are taken from the calibration.
9) Select the ion pairs for one of the compounds to be monitored and then click on XIC (extracted ion chromatogram). An additional pane will open with all of the selected ion pairs displayed in different colors. The pane provides real time concentrations with the vertical axis scaled in parts per billion (ppb) or other units as selected during calibration. (Figure 7.7.6).

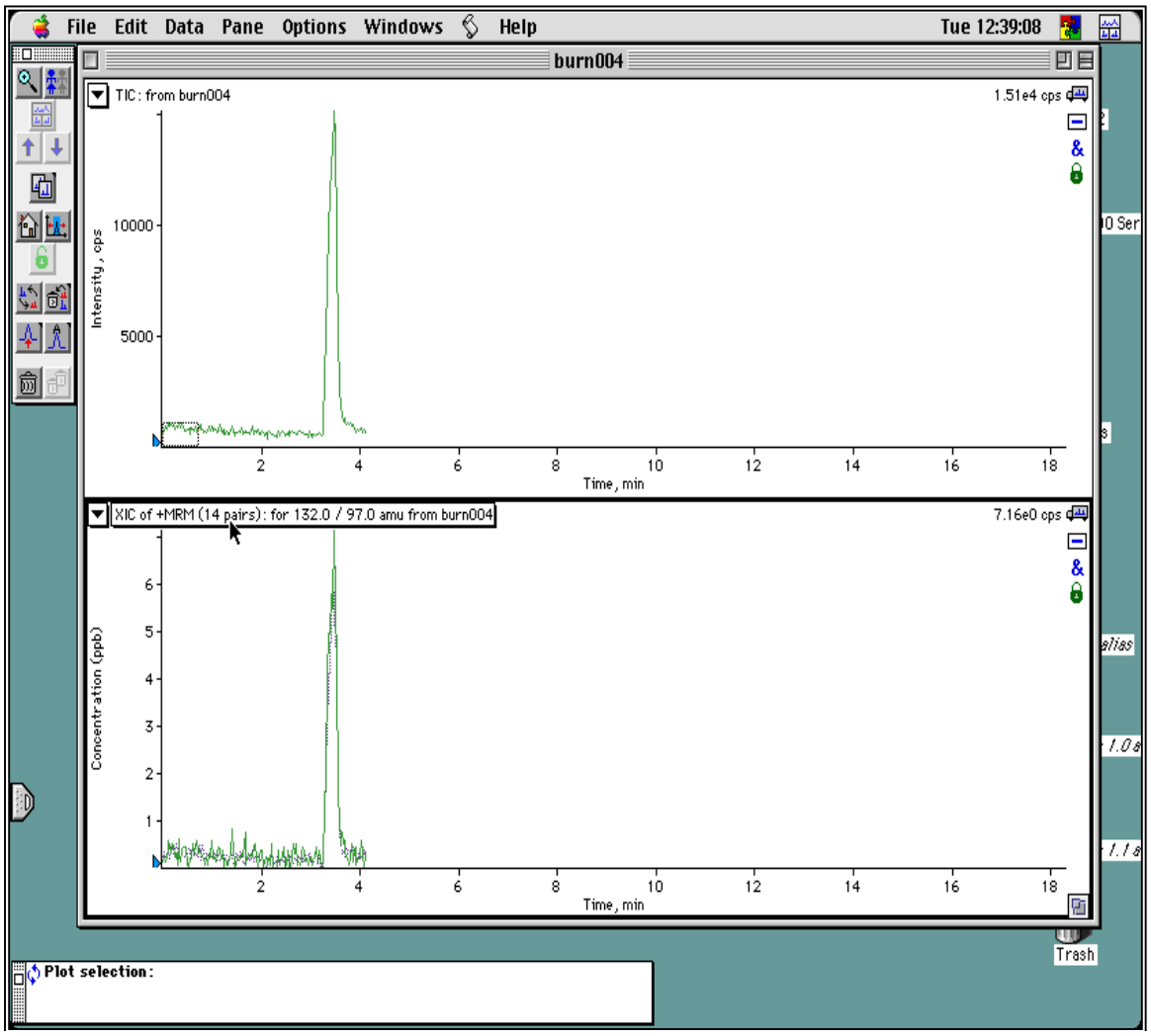

Figure 7.7.6 Real Time Quantitative Display

10) The XIC trace shown as a solid line is the one identified in the rectangle at the top of the pane. All of the other selected ion pairs are shown as dashed lines. To select another solid line XIC, put the cursor on the ion pair at the top of the pane and click the left mouse button. All of the ion pairs will show. Move the cursor to the new selection and release the mouse button. The new selection will now be identified as a solid line (Figure 7.7.7).

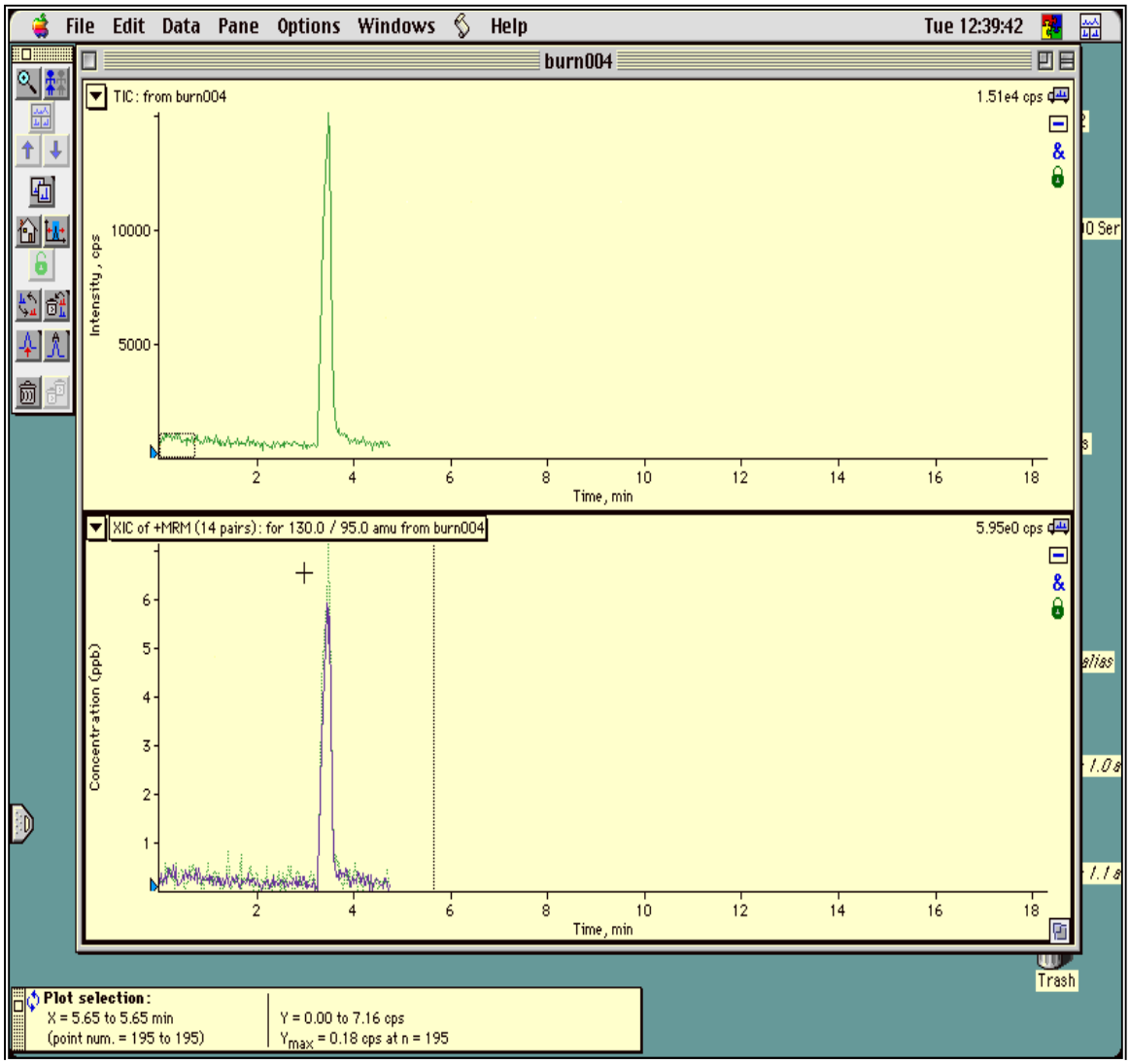

Figure 7.7.7 Selection of Highlighted Ion Pair

11) **TO SET FLAGS:** At the menu bar → click the Script icon (Figure 7.7.7). Click [FLAG EVENT]. The Flag Event pane will appear, superimposed on the Multiview pane (Figure 7.7.8). Enter the appropriate text (usually one or two uppercase letters) to appear as the flag, click [OK] (or press ENTER on the keyboard).
12) The flag dialog box will still be active on the screen, and a blue highlight will be covering the flag text box. **Do not hit ENTER again, or another flag will be set with the same letter. Note:** If the operator clicks on another pane after bringing up the FLAG EVENT pane, the pane will disappear from view, but is not closed. Click on the upper right square at the corner of the screen (the dialog box). All of the active panes will be listed. Move the pointer to FLAG EVENT, and the pane will reappear on top of the others.

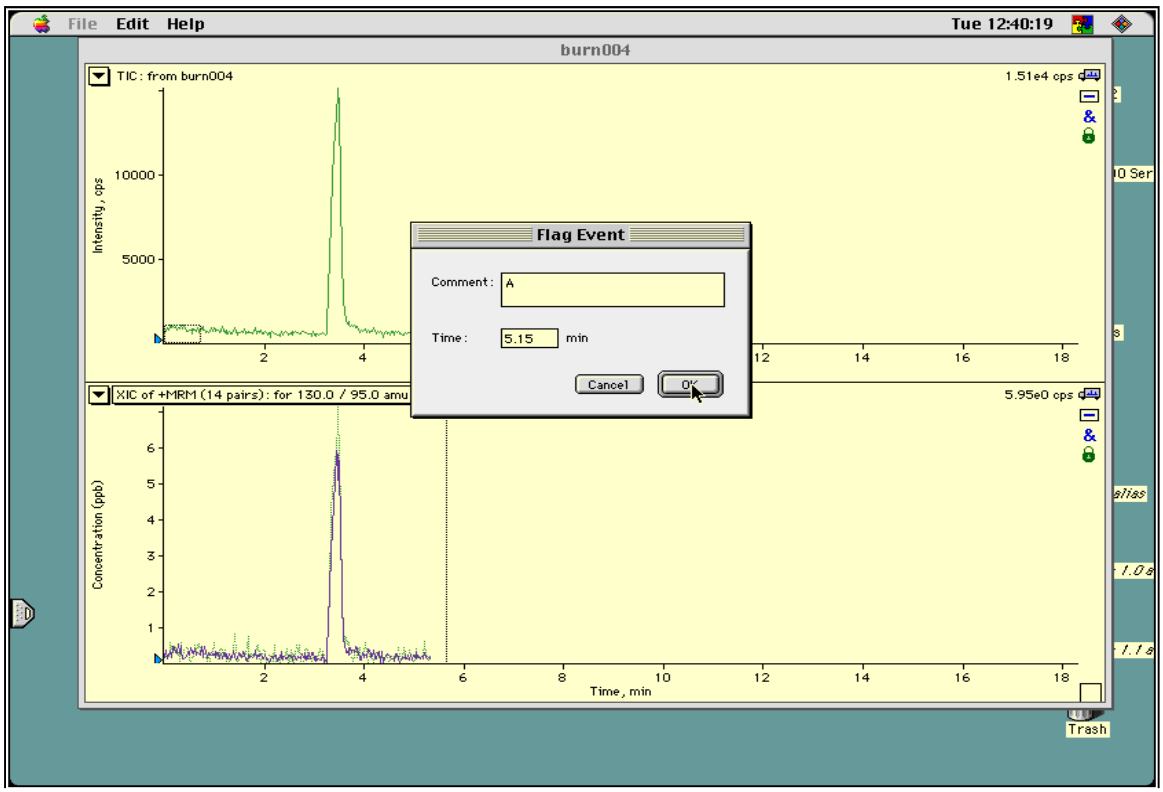

Figure 7.7.8 Setting Flags

13) Enter the appropriate text, the next flag; click [OK] (or press ENTER on the keyboard) to set the flag. The dialog box will disappear.
14) Repeat steps 11 through 13 to set more flags during the acquisition.
15) Figure 7.7.9 present example of entries made in an Event log during a monitoring survey. The time entered in the log was obtained from the Status Windows at the moment the flag was entered.

TAGA Analysis Event Log

Date: March 28th 2005	Time: 15:35:46	Operator's Initials: TAA
Analysis Type: MRM	TAGA Filename: GTOS056	Source Pressure (torr): 1.8

TAGA File Title: GTOS NORRIS SURVEY 1

Flag	Time	Comments/Locations/Intersections/Landmarks/Sources
A	00:31	~~Enter Building~~ Start Ambient
B	1:32	~~Start~~ End Ambient
C	2:29	~~End~~ Enter Building
D	5:35	Start Room 44A
E	6:35	End Room 44A
F	6:55	Start Room 44
G	7:56	End Room 44
H	8:23	Start Room 43
I	9:23	End Room 43
J	9:51	Start Room 43 Closet
K	10:51	End Room 43 Closet
L	11:41	Start Room 45
M	12:41	End Room 45
N	13:15	Start Room 46 (Men's Bathroom)
O	14:15	End Room 46 (Men's Bathroom)
P	14:31	Start ~~Roo~~ Floor Drain in Room 46
Q	15:32	End Floor Drain in Room 46
R	16:00	Start Room 42
S	17:01	End Room 42
T	17:26	Start Room 41
U	18:27	End Room 41
V	19:33	Start Women's Room (# 47) # missing
W	20:33	End Women's Room
X	20:40	Start Floor Drain in Women's Rm
Y	21:40	End Floor Drain in Women's Rm
Z	22:24	Start Room 48

Recommendations:

Figure 7.7.9 TAGA Event Log for Monitoring Surveys

16) To abort or end the run, select [TAGA EXPRESS] in the upper right dialog box. At the menu bar → [FILE], [ABORT].
17) Click on the TIC display. At the menu bar → [FILE] [PRINT] [PRINT].
18) Staple print out to the Event Log page and place in daily folder.
19) Click on the square in the upper left corner of the TIC pane to close the file.
20) Repeat process from step 1 until all monitoring acquisitions are completed.
21) Data will be processed as per SERAS SOP #1743, or as instructed by an experienced data processer.

7.7.3 Monitoring Types

1. **Stationary Monitoring** is usually performed to provide the concentration profiles for targeted compounds at specific locations. It may be performed with or without the 300-foot exterior Teflon hose. If the hose is not used, particular attention must be given to the location of the generator exhaust and the TAGA inlet relative to the prevailing wind. The TAGA inlet should not be downwind of the generator exhaust. If the 300-foot hose is used, transport efficiency must be demonstrated at the beginning and end of each monitoring day. Concurrent with stationary monitoring, meteorological conditions are usually recorded. The location of the TAGA inlet should be carefully noted for each monitoring period for later use in providing the monitoring location in relation to the site map.

2. **Mobile Monitoring** is usually performed to identify and locate plumes of targeted compounds. Flags are set at each turn or significant landmark, and additional flags may be set if significant plumes are encountered. Since the Global Positioning System (GPS) is usually operated during these runs, it is important to set the TAGA computer's clock time accurate to the nearest second. The correct time may be taken from the GPS. This allows coordination of geographic positions with the TAGA flags.

3. **Building Surveys and Investigations** a calibration is usually performed immediately prior to monitoring the first building each day. Depending on a variety of parameters, it is normal to perform three calibrations during the monitoring day, one before the first building, one during the middle of the day, and one after the last building. The transport efficiency is measured after the first and last calibration of the day. Prior to monitoring operations, the field crew enters each building and a rough drawing is sketched, along with dimensions, and the rooms and landmarks are named. These names are used when monitoring the building, and the flag identifications are noted on the drawing during monitoring and checked immediately subsequent to monitoring. The TAGA file name is included on the drawing.

- A member of the crew places one end of the Teflon sampling hose at the ambient background position, and the other end of the hose is connected to the TAGA inlet.
- Check radio communication with crew member responsible for entry into the structure to be monitored.
- Begin a monitoring run as in Section 7.7.2.
- Display the concentrations of the substances of concern on the screen with [USE

CALIBRATION] and select the ions, then [Show XIC].

- Flag the beginning and end of the ambient monitoring period, usually at least one minute.
- Notify the hose operator that the ambient is finished, and the building may be entered.
- Flag the time the building is entered.
- The field sampling person moves the hose inlet about the building, one room at a time. When he gets to the center of each room, he notifies the TAGA operator. The TAGA operator then flags the event and notifies the hose operator. The TAGA operator then notifies the hose operator when the one-minute monitoring period is finished so he can move on, and flags that event. The TAGA operator may decide to extend the one minute monitoring time for each location if the time to complete each sequence exceeds one second (to assure a large number of sequences incorporated into the average), or if there is a significant change in concentrations being monitored, to allow for equilibrium to be reached in the hose.
- Once the interior monitoring is completed, the hose operator exits the building and returns the inlet end of the hose to the ambient location. The TAGA operator flags the return to the ambient location and flags the beginning and end of a one-minute ambient monitoring period. Once the ambient monitoring period has been completed, the TAGA operator spikes the inlet with 30-mL/min of standard for one minute.

7.8 Data Evaluation Routines

There are multiple software routines available to aid in evaluating the data while it is being acquired and/or after data has been collected. Procedures for some of the more useful routines are described below.

7.8.1 Calculating Average Concentrations during an Acquisition

1) Open EXCEL if not currently open.
2) Click on the TIC for current acquisition. At the menu bar, click on the Script icon, select [USE CALIBRATION].
3) Select the ion pairs to be included in the calculation.
4) Enter the beginning and end times for the period for which the average concentration is to be calculated.
5) Click [GENERATE REPORT].
6) The software will generate an EXCEL spreadsheet which provides the average concentration for each compound and each ion pair, along with their standard deviations.

7.8.2 Marking Threshold Limits

TAGA MultiView software has the capability of allowing the operator to set threshold limits and indicate portions of the XIC trace above the selected level. While this can be done for TIC or raw extracted ion pairs, it is most useful when done for ion pairs quantified under "USE CALIBRATION".

1) At the menu bar, click on the Script icon, select [USE CALIBRATION]. Highlight the ion pairs of interest. Click [Show XICs] (Figure 7.8.1).
2) Click and drag the blue triangle at the Y-axis origin up to the selected level.

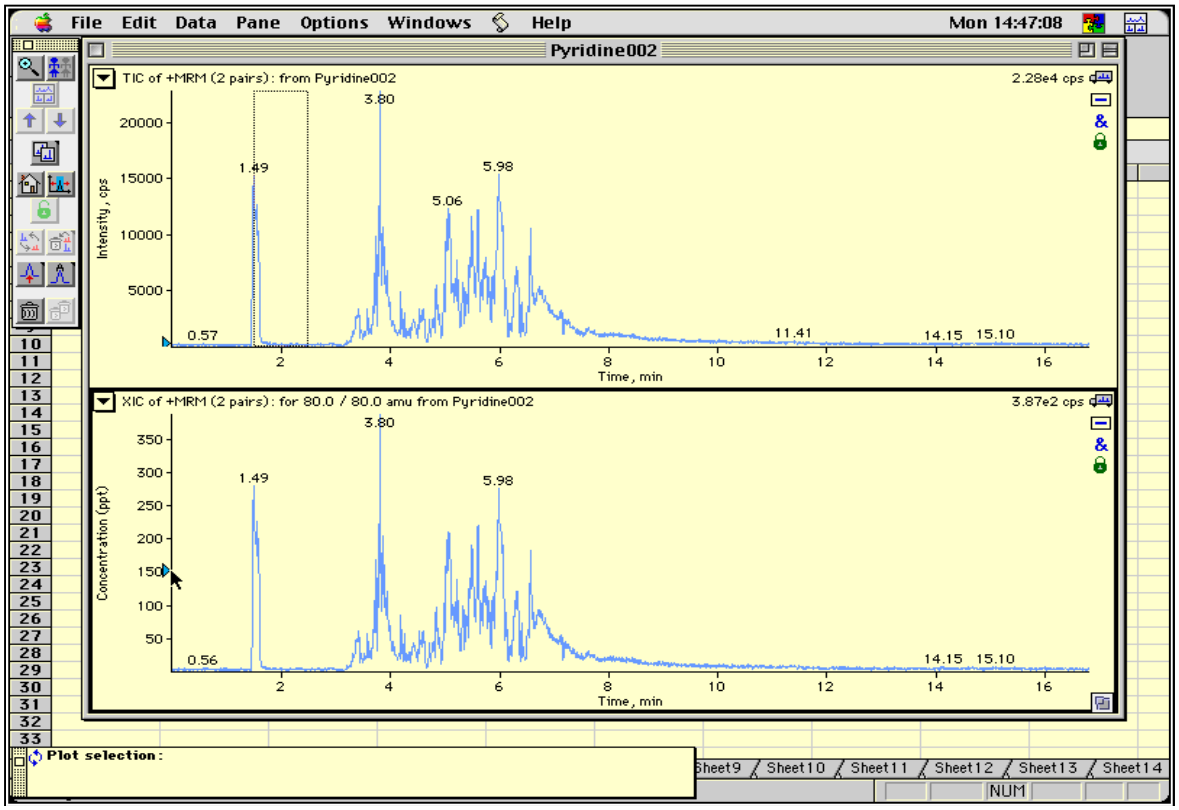

Figure 7.8.1 Select ion pairs and set threshold level

In Figure 7.8.1, the threshold is set for 150 parts per trillion (ppt) for the parent ion pair for pyridine. **Note:** in this example, the actual quantitation limit was close to 10 ppt, but the level of concern (action limit) was significantly higher than the quantitation limit for this particular work assignment.

3) Select the area of concern in the XIC (click and drag through the area). This marks the selected area in a blue box (Figure 7.8.2).

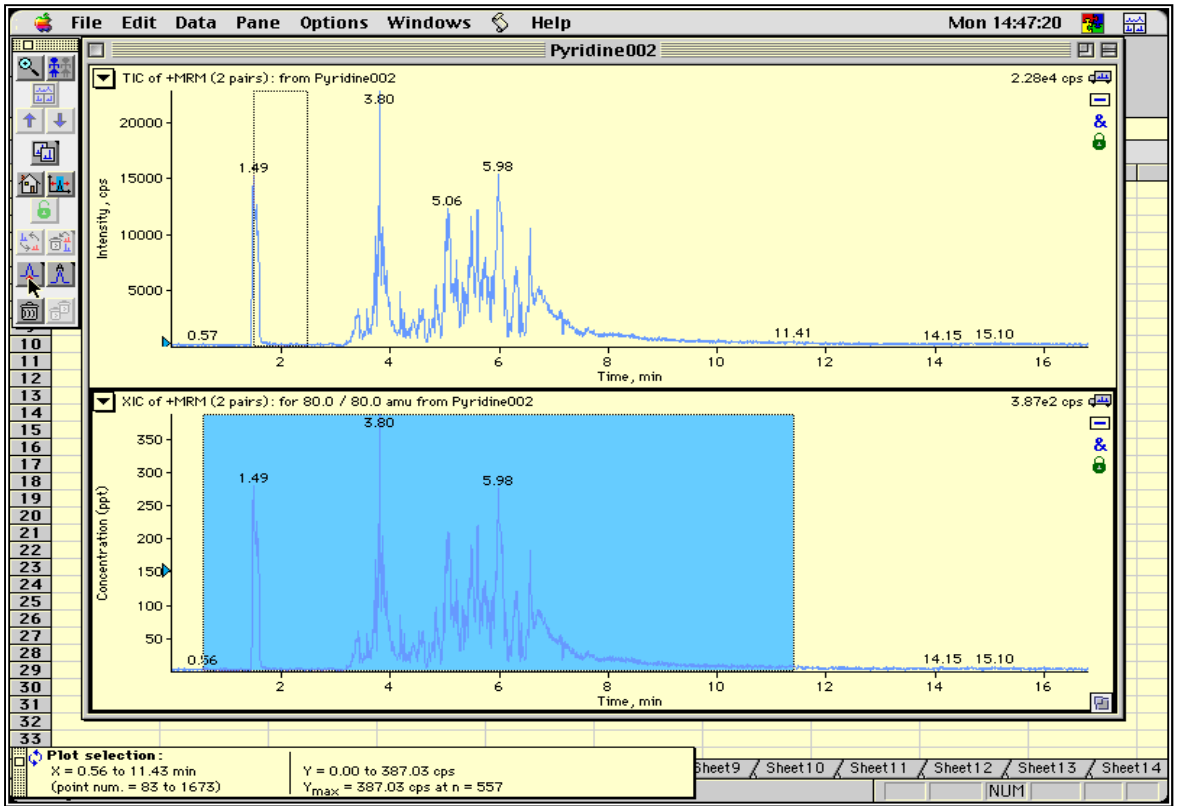

Figure 7.8.2 Selecting the Area of Concern

4) While holding the "action key" (the one with the "~" tilde mark), select the icon, the chromatographic peak with the red arrow under it, from the left pane menu (as seen with the cursor arrow, above).

5) Clicking on the icon will mark the areas of the chromatogram above the selected threshold (Figure 7.8.3).
6) Clicking on the icon right next to it, chromatographic peak with an "A" above it will provide the time into the acquisition for each peak above the selected threshold.

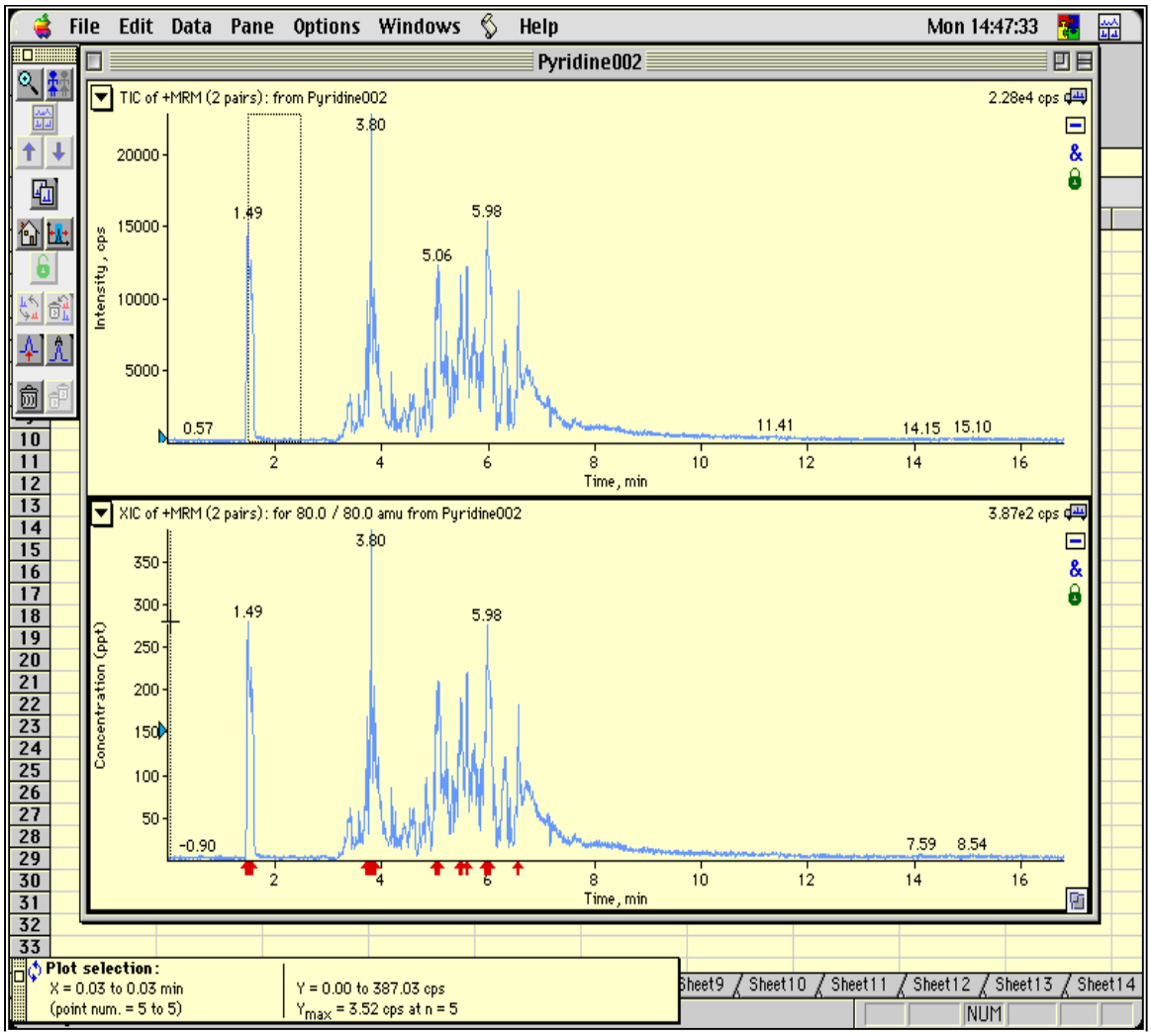

Figure 7.8.3 Marking Portions of Chromatogram above Threshold

7.9 MRM Table

The "MRM Table" file, a tab-delimited Excel spreadsheet, is a listing of compounds and their respective parent and daughter ions. **It is located in the following directory: /System Folder/Preferences/ECAf.** This file is used in various applications, such as "Use Calibration" and "Create Calibration", used to identify and quantify compounds.

It is imperative that the following be strictly maintained:

- **The file must be saved as a text (tab delimited) file**, and must retain the name "MRM Table". If there are any changes to these, the applications that use this file will not be able to find the file and will abort.
- When making any compound updates or additions, maintain the same entry format.
- Listing of compound ion pairs must be together in the table.
- Names are case sensitive; therefore, to maintain consistency enter all compounds in upper case.
- The names must be an exact match with the names used in the concentration tables. **Note:** spaces, before or after the name, are significant.
- The compound name and parent/daughter ion pairs must be present in the MRM table in order for the software to identify the ion pair correctly. Refer to Table 1, Appendix B. Column B of the MRM Table is used for identification. It is best to use short abbreviations in this column.

7.10 Concentration Tables

Concentration tables are tab-delimited text tables used by the software to calculate calibration curves. The concentration table is comprised of concentration columns selected to match the concentration steps in the calibration. There is a separate concentration table for each compound, and the name of each concentration table must be the name of the compound, and that name must match the name of that compound in the MRM Table exactly. The names are case sensitive, and both leading and trailing spaces are significant. Additionally, the order of the concentrations in the concentration table must match the order of the levels selected when creating the calibration.

For ease of calculation, a set of Excel spread sheets is provided in a directory called Calculation Aids. Some of the files are named for specific calibration standard cylinders. If a new calibration standard cylinder is put on the mobile laboratory, copy one of the existing files, and re-name it for the new cylinder number. The detailed procedure is as follows:

7.10.1 Creating Concentration Tables

- Open Excel
- Enter the concentrations in a vertical column, in the order in which the concentration levels will be selected when creating the calibration.

Save the file under US EPA2/System folder/Preferences/ECAf/Concentrations as a **Tab delimited text file**. The name of the file must exactly match the name of the compound in the MRM Table.

7.10.2 Modifying Concentration Tables

1) Load EXCEL, at menu bar → **[FILE] [OPEN]. Go t**o directory, US EPA2 → Calculation Aids, and open the appropriate file, for example; file "cc250186conc.xls" (Figure 7.10.1).

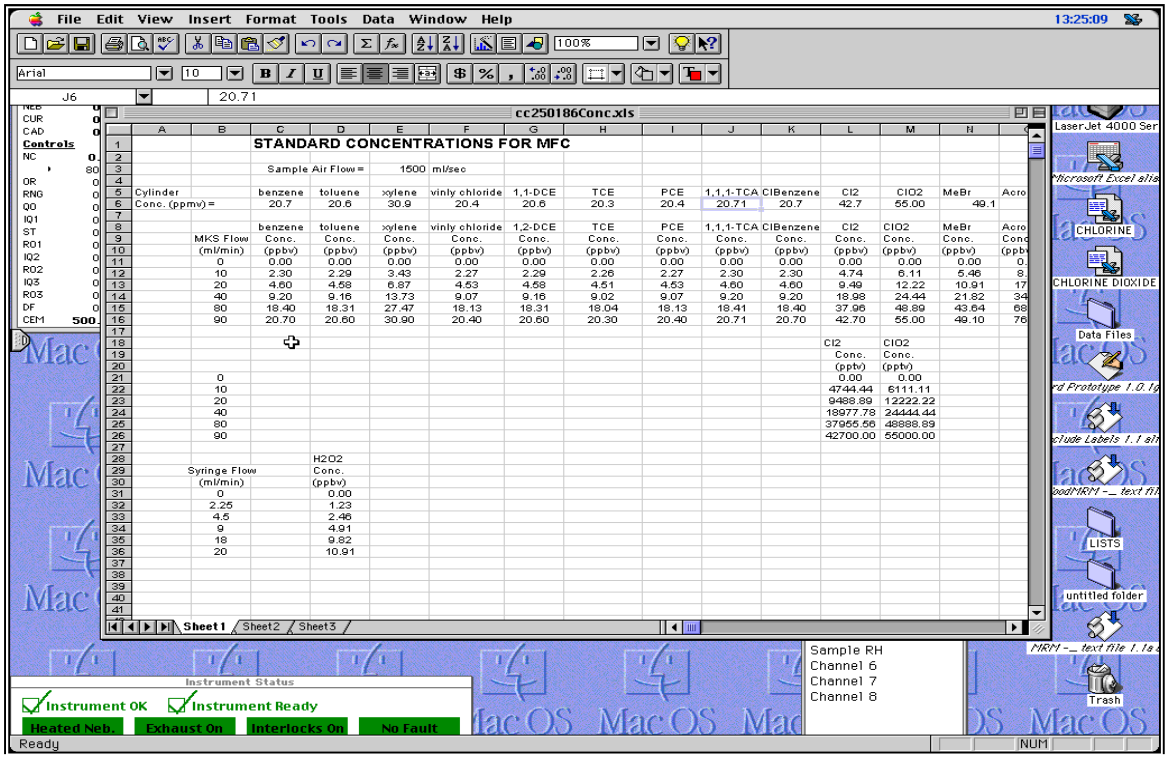

Figure 7.10.1 Cylinder Concentration File

2) In cell "E3", enter the SAF value, in mL/sec, that will be used for the calibration.
3) In row 6, enter the concentration of the compounds found in the cylinder certification as provided by the manufacturer in the appropriate cells. Line 6 is labeled "Cylinder Conc. (ppmv) =".
4) In column "B", under the label "MKS Flow (ml/min)", enter the flow rates, in mL/min, that have been set to used for the standard gas flow rates during calibration.
5) As values are entered in steps 2 thru 4 compound concentrations will be re-calculated for each calibration level.

6) While leaving the current Excel file open, open the Concentration Table file for one of the compounds (Figure 7.10.2). At the menu bar, [FILE] [OPEN] → go to the following directory: US EPA2/System folder/Preferences/ECAf/Concentrations.

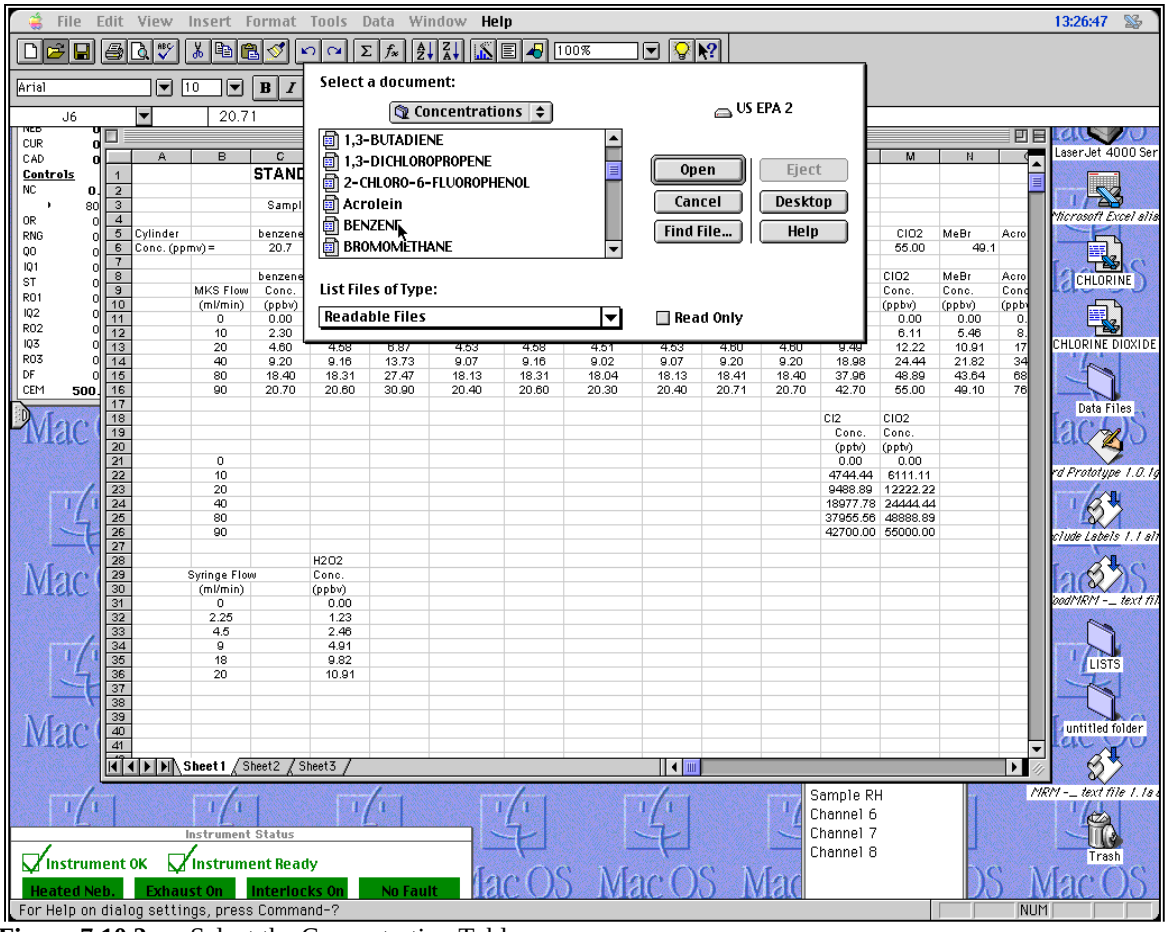

Figure 7.10.2 Select the Concentration Table

7) The "Text Import Wizard" dialog box will open, click on [FINISH]. (Figure 7.10.3). For this example, the compound benzene is being used.

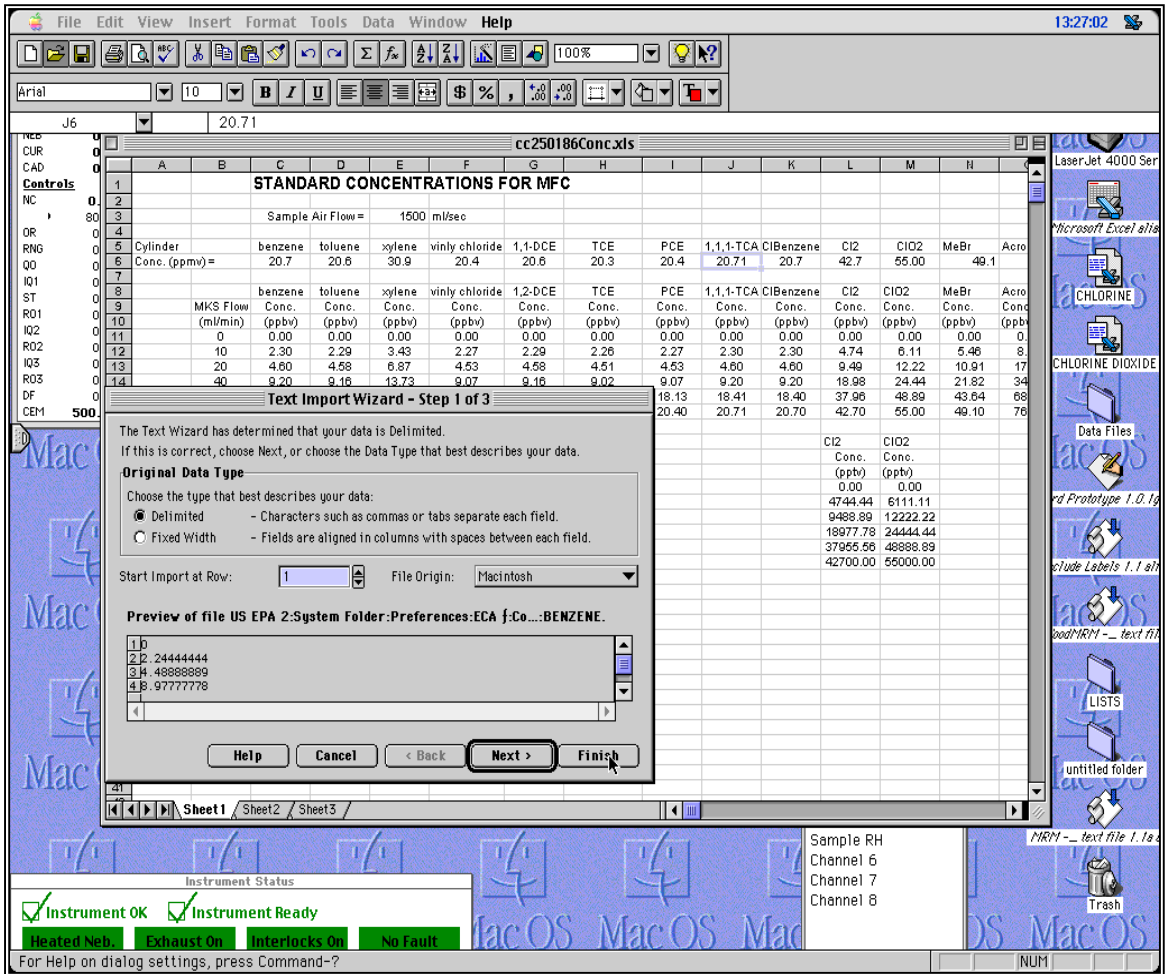

Figure 7.10.3 Selecting the Concentration Table

8) This opens an Excel file with the concentration table for benzene. **Note:** this file will be in a tab delimited text format.
9) Minimize this file, preferably so that only columns A and B, and rows 1 to 10 are visible. This can be accomplished by placing and clicking the cursor on the bottom right corner of the file and dragging in until the desired size has been achieved.
10) Click on the still open Cylinder Concentration file, i.e. cc250186Conc.xls.

11) Highlight the concentrations of the selected compound, at the menu bar, → [EDIT] [COPY] (Figure 7.10.4).

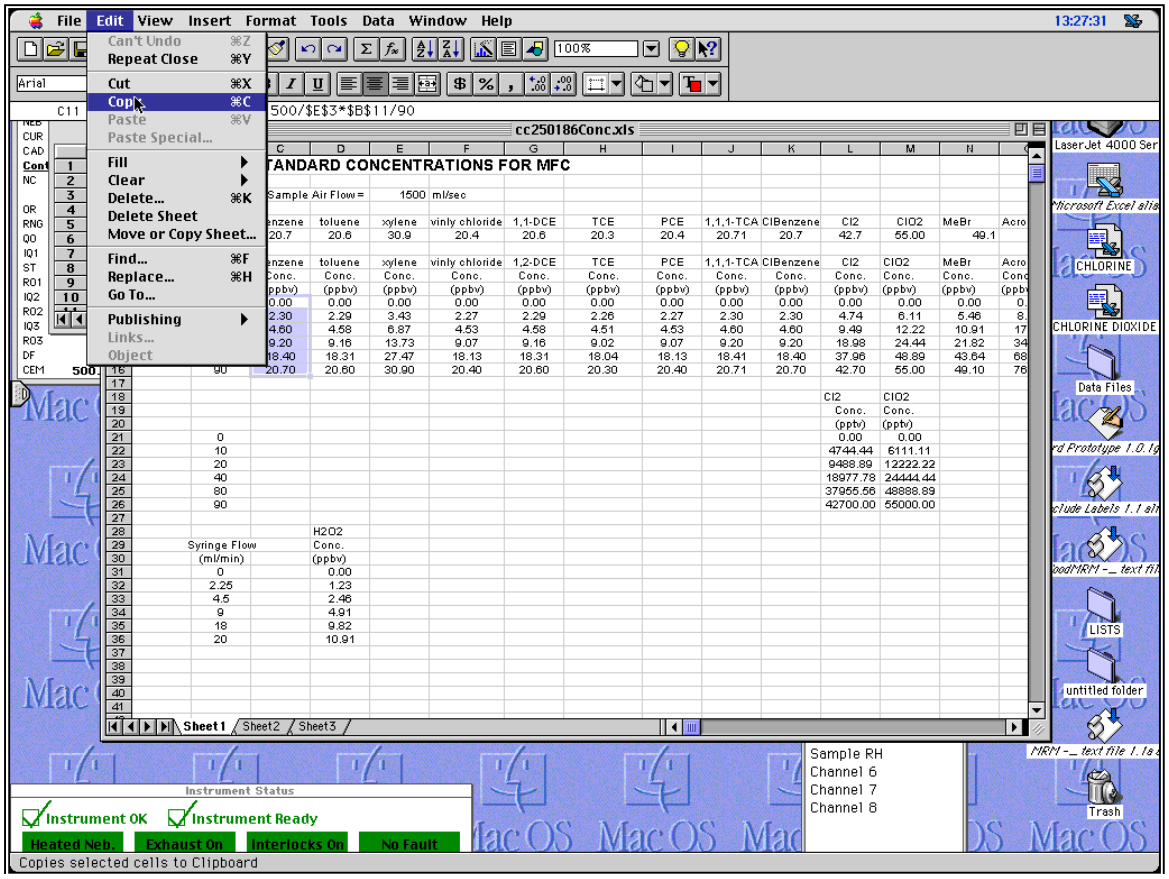

Figure 7.10.4 Copy the Compound Concentrations

12) Click on the minimized Concentration Table, benzene in this example.
13) Click into cell A1. At the menu bar, [EDIT] [PASTE SPECIAL]. (Figure 7.10.5)

14) Dialog box will open. Choose “Values” in the Paste section, then click [OK] (Figure 7.10.5).
15) This will paste the actual concentration values rather than the formulas that are in the Cylinder Concentration file.

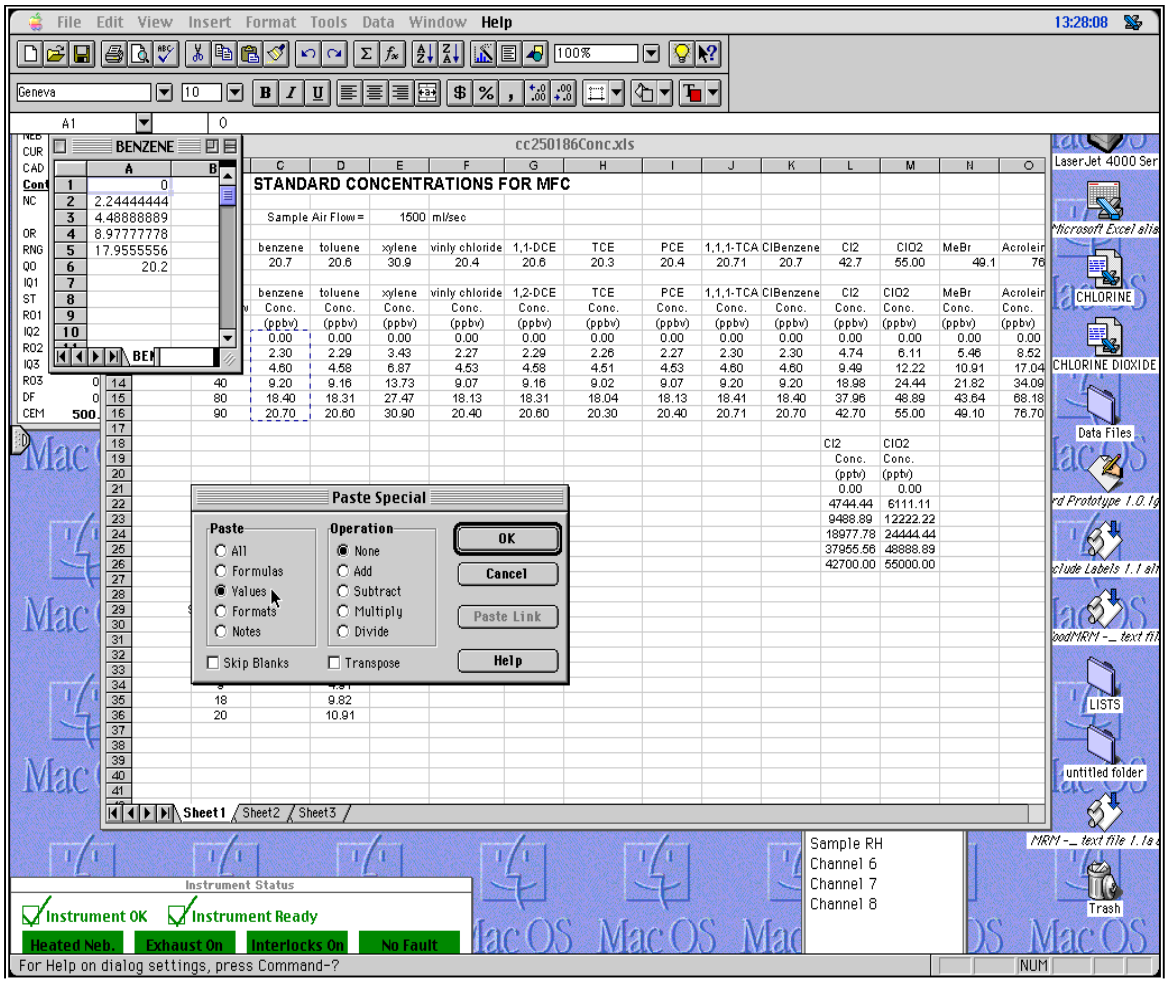

Figure 7.10.5 Paste New Concentration Values into the Table

16) At the menu bar, [FILE] [SAVE AS] (Figure 7.10.6). Go to the following directory: US EPA2/System folder/Preferences/ECAf/Concentrations.
17) Ensure that "Text (Tab delimited)" is chosen in "Save File as Type:"

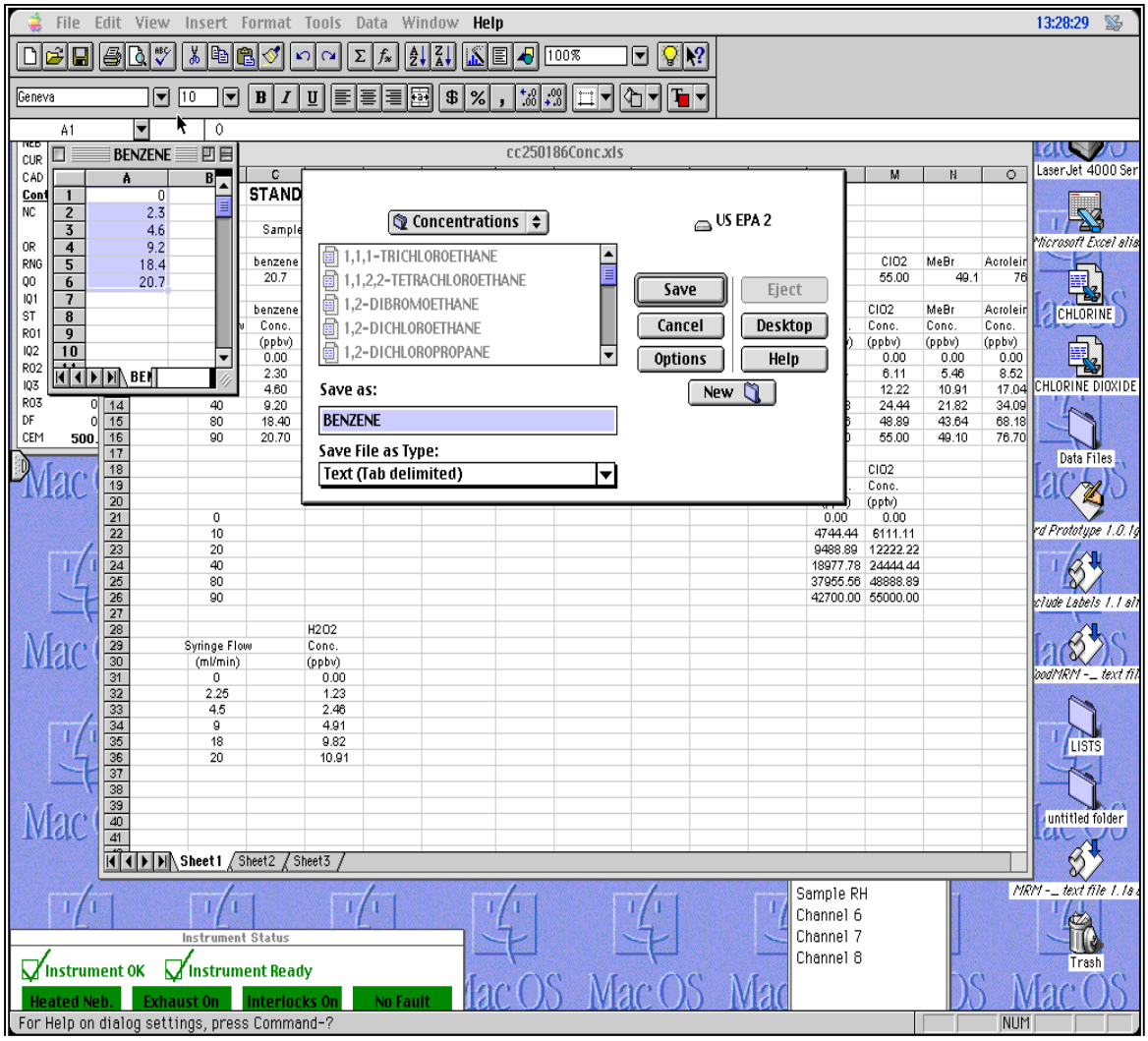

Figure 7.10.6 Saving as Tab Delimited Text File

18) Click [SAVE].

19) Close the Concentration Table by clicking the square in the upper left corner of its frame.
20) Excel will give the option to save the file again. **ALWAYS c**lick [NO] (Figure 7.10.7). **If [YES] is chosen, EXCEL will re-save the file in another format, and the Concentration Table for the compound will not be found by the calibration software.**

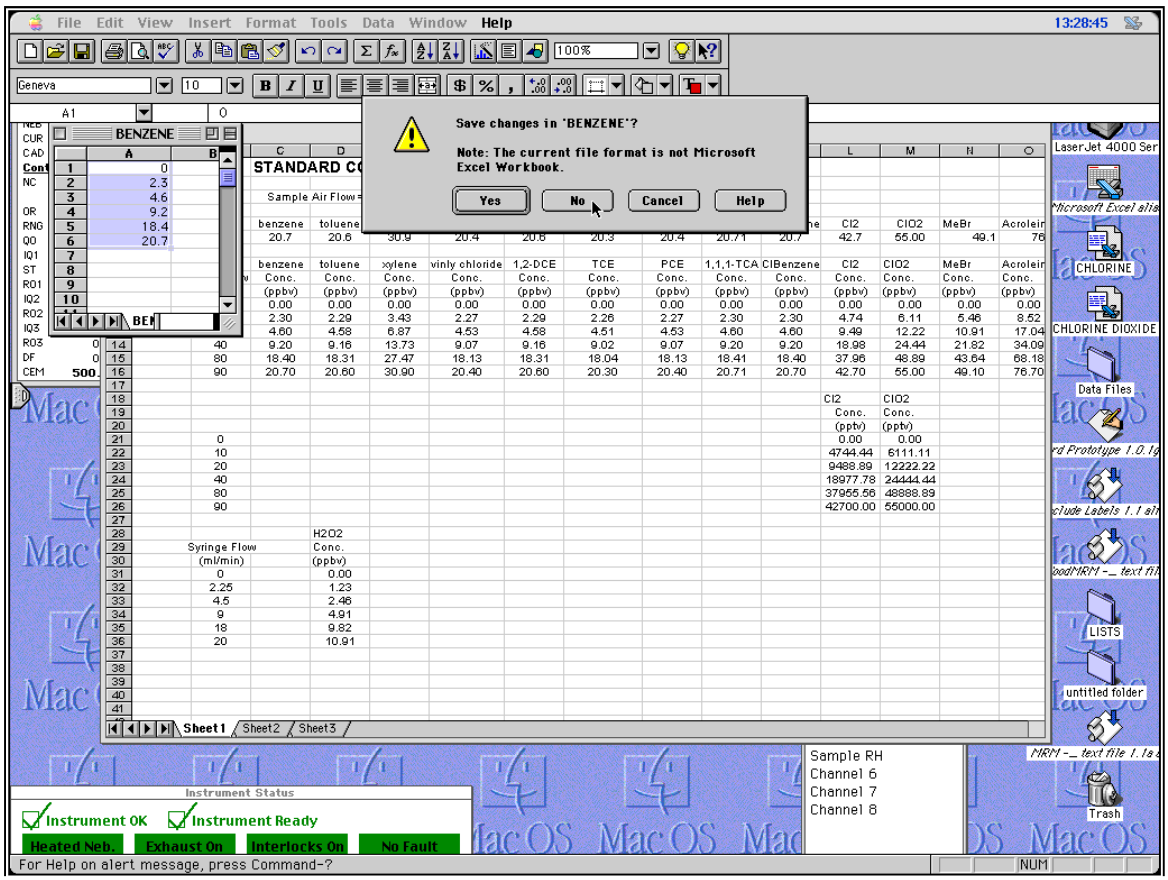

Figure 7.10.7 Exiting the Concentration Table

21) Repeat steps 6 through 21 for all compounds to be calibrated.
22) When all compound Concentration Tables have been updated and saved, close the Cylinder Concentration file by clicking on the square in the upper left corner of its frame.
23) New data can be saved, but is not necessary since this file is just concentration calculation aid.

7.11 Experiment File

The Experiment file is created for targeted compounds and is used by tuning applications and calibration and monitoring methods. An Experiment file can be created in Tune or Sample Control. Tune allows the use of only eight ion pairs in an Experiment file. An Experiment file created in Sample Control will accommodate the use of many more ion pairs.

7.11.1 Modify Experiment File in Tune

1) Determine and list all compound and the ion pairs to be used for acquisition.
2) Click on the Apple icon, and then click on [TUNE] to load Tune application.
3) At the menu bar, select [File] → [Open Experiment]. Select an existing Experiment to be modified from directory: US EPA (1 or 2)/Instrument/exp.
4) At the menu bar, select [File] → [Save Experiment As], and rename the Experiment file (Figure 7.11.1). **Be sure to do this before modifying the old experiment.**
5) Click [Save].

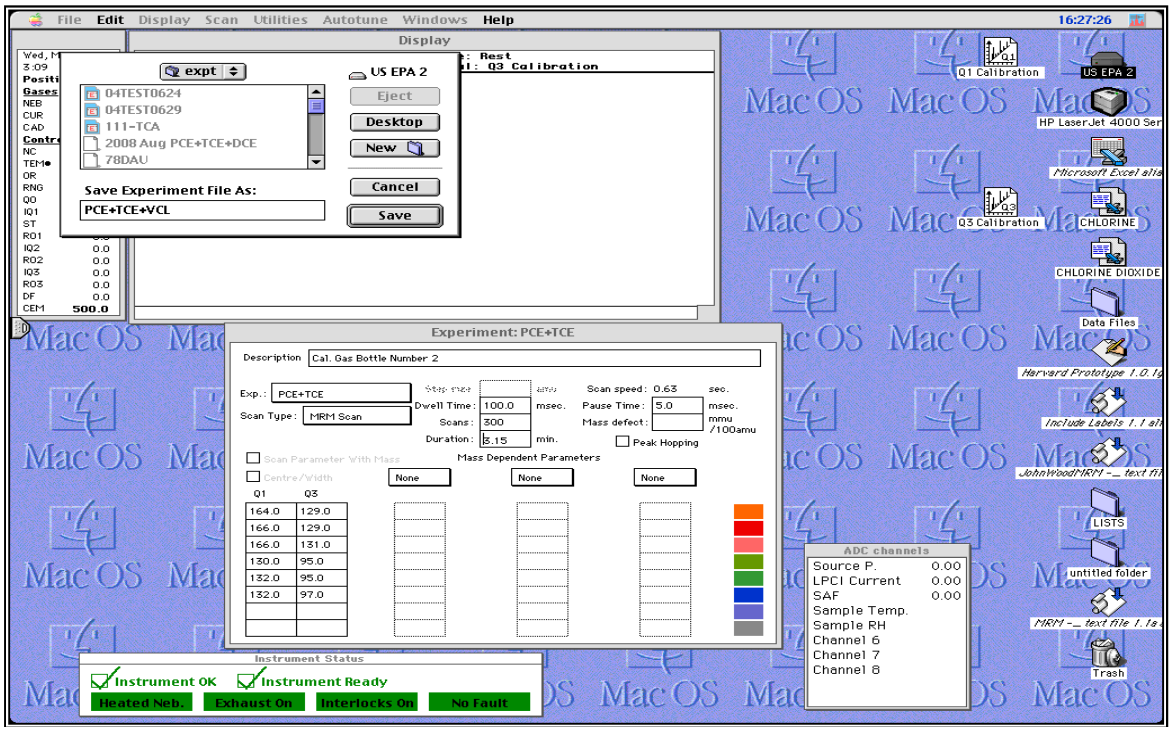

Figure 7.11.1 Renaming the Experiment file

6) At the menu bar, select [Scan], ensure that [Q2 Purge] is not checked (Figure 7.11.2).

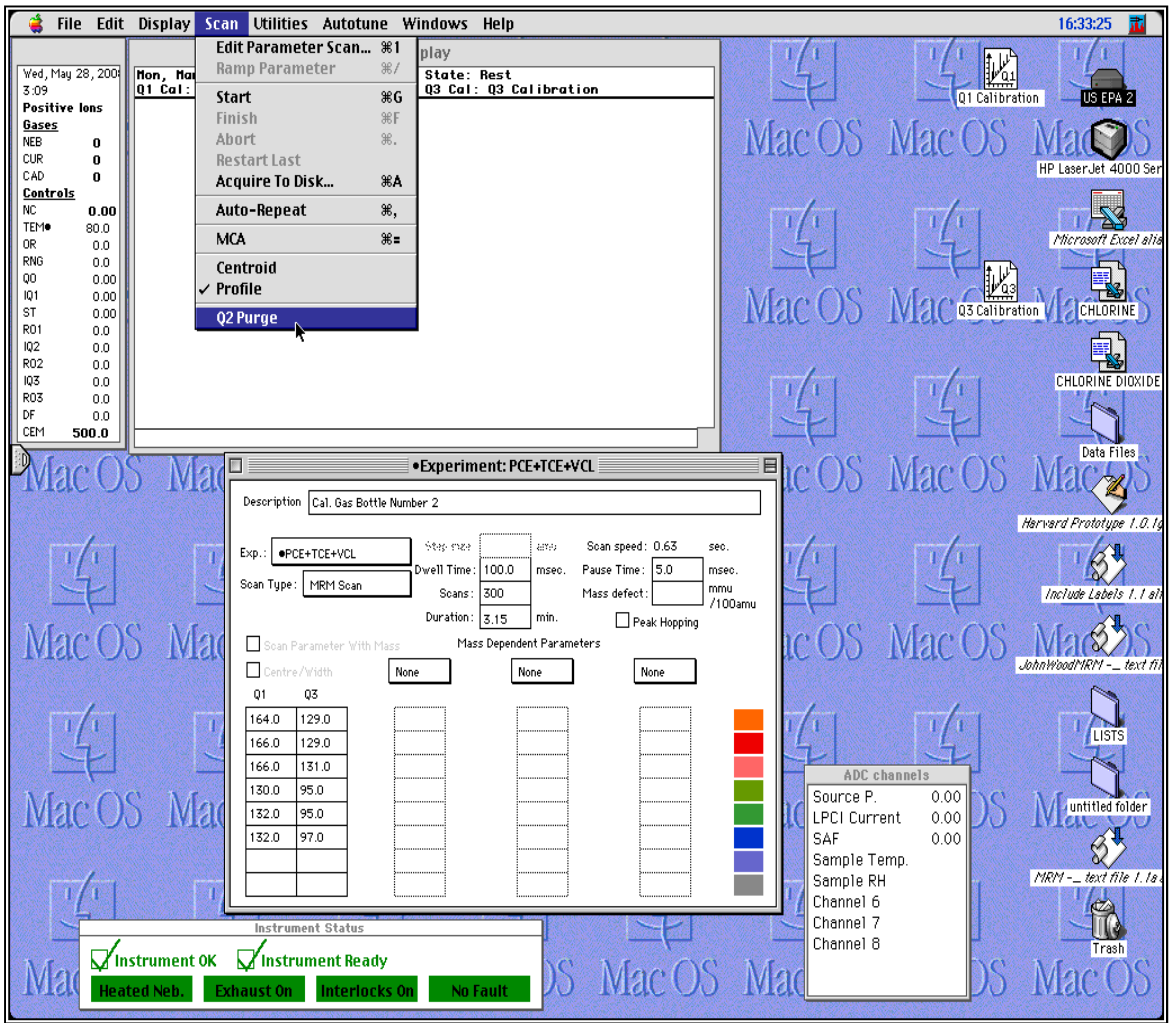

Figure 7.11.2 Q2 Purge

7) Modify or add ion pairs to the columns labeled “Q1” and “Q3”.

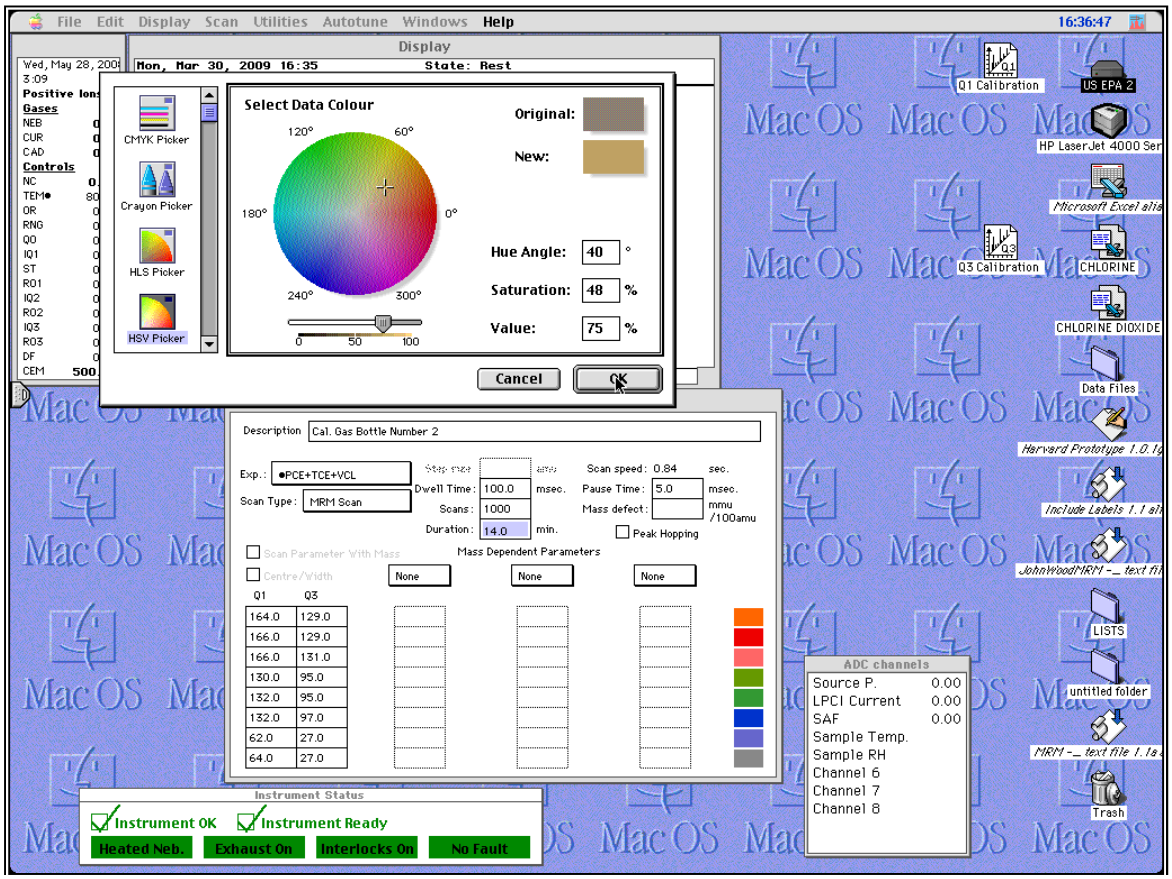

Figure 7.11.3 Modifying Parameters of the Experiment File

8) Modify all parameters, such as Scan Type, Dwell Time, Scans, etc., as needed for the new experiment (Figure 7.11.3).
9) The color for each ion pair can be modified by clicking in the corresponding box in the last column. This opens the color dialog box as in Figure 7.11.3. Click [OK] when desired color has been achieved.

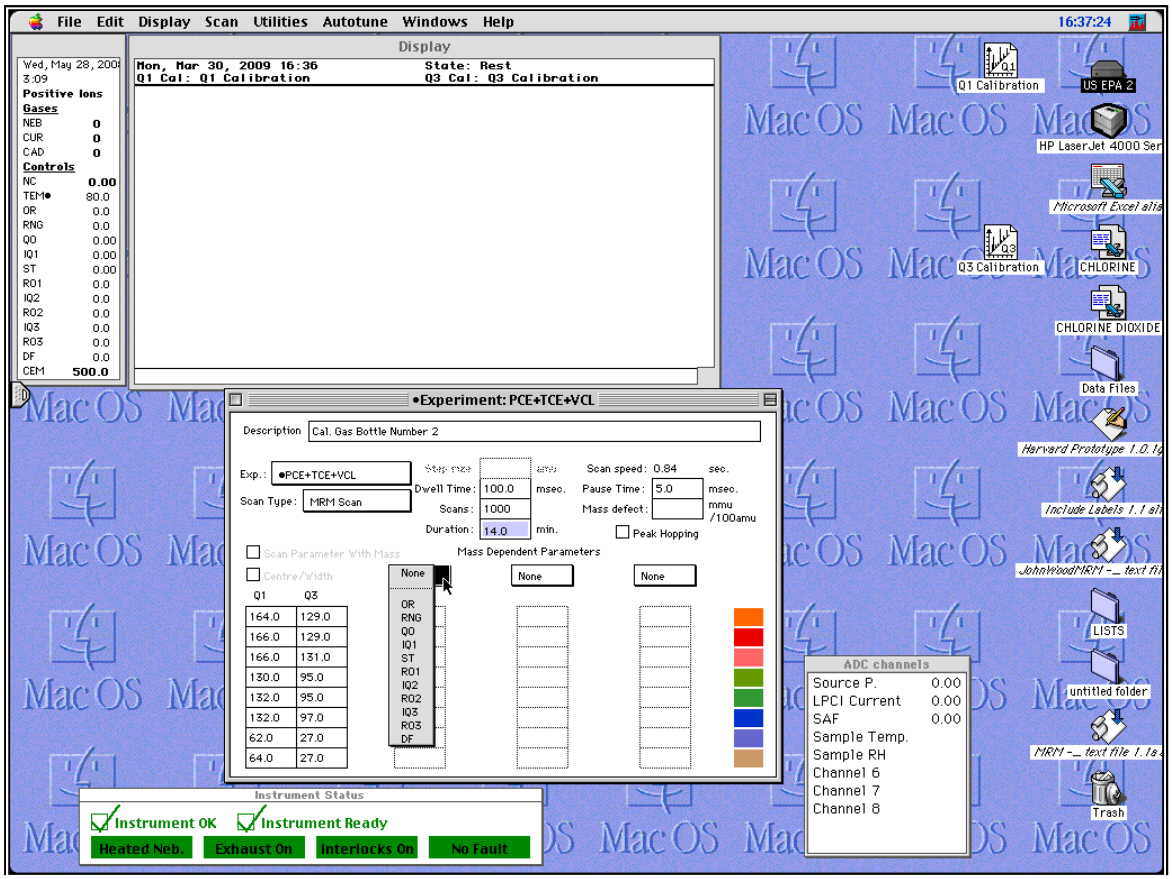

Figure 7.11.4 Assigning Specific Tune Parameters to Individual Ion Pairs

10) Specific values for Tune parameters can be assigned to individual ion pairs (Figure 7.11.4).
11) When all modifications and updates have been completed, at the menu bar, [File] → [Save Experiment].
12) Ensure that file is saved in the proper directory, Instrument/experiment, and has the current name.

7.11.2 Create Experiment File in Sample Control

Experiments created in Sample Control are different from those created in Tune. They can accommodate many more ion pairs than the eight ion pair maximum of Tune.

1) Determine and list all compound and the ion pairs to be used for acquisition.
2) If TAGA EXPRESS has not already been loaded, at the menu bar, click the Apple icon at the upper left, click [TAGA EXPRESS]. This loads both TAGA EXPRESS and Sample Control. Alternatively, click the Apple icon at the upper left corner, then click [SAMPLE CONTROL]. This loads Sample Control directly, but does not load TAGA EXPRESS.
3) In Sample Control frame, click on [Expt Editor] icon to open Experiment Editor (Figure 7.11.5).

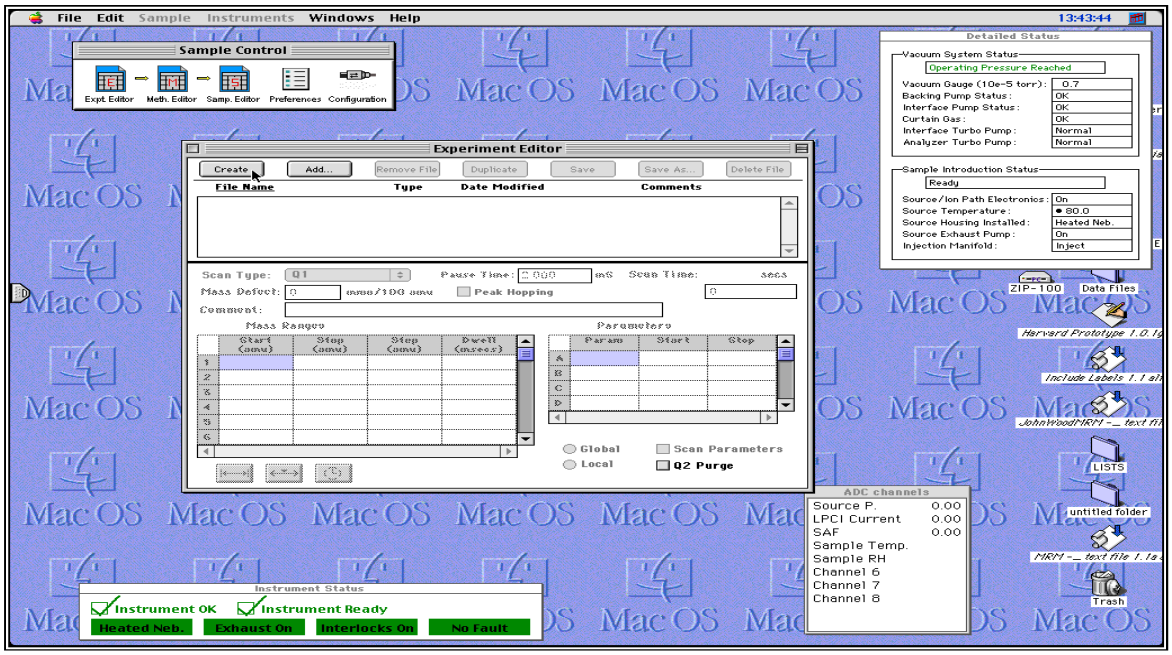

Figure 7.11.5 Experiment Editor

4) The initial Experiment screen will appear with options to create a new experiment or add an existing one. If modifying an existing Experiment, select [ADD] → choose the experiment to modify, click [ADD] [DONE].
5) Immediately save the Experiment under a new name. At the menu bar, [File] [Save Experiment As]. Ensure appropriate directory: US EPA (1 or 2)/Instrument/Experiment and type in new name.

6) Modification of the Experiment can proceed as needed. Save modified experiment when completed.
7) To create a new Experiment, go back to step 4 and select [CREATE].
8) Ensure that the Q2 Purge box in the lower right corner of the Experiment Editor is not checked (a check mark at Q2 Purge is the default mode). Click on the checkmark in the box beside Q2 Purge to un-check it.
9) For the purposes of this example, at "Scan Type", select MRM from the drop down menu. The other choices are Q1, Q3, Product, Precursor, and Neutral Loss
10) Enter 5.0 (mS) in the "Pause Time" box. Enter a description for the experiment in the "Comment" box.
11) In the "Mass Ranges" section, enter at least the first ion pair in the Q1 and Q3 columns, and the Dwell Time (usually 100 msecs),
12) Click [Save]. Make sure to be in the appropriate directory: US EPA (1 or 2)/Instrument/Experiment. Enter the desired file name and click [SAVE].
13) In the "Mass Ranges" section, continue to enter the ion pairs and their dwell times.
14) The default maximum number of ion pairs is 20. If more ion pair entries are required, click on the line number of one of the ion pairs highlighting the entire line (Figure 7.11.6).

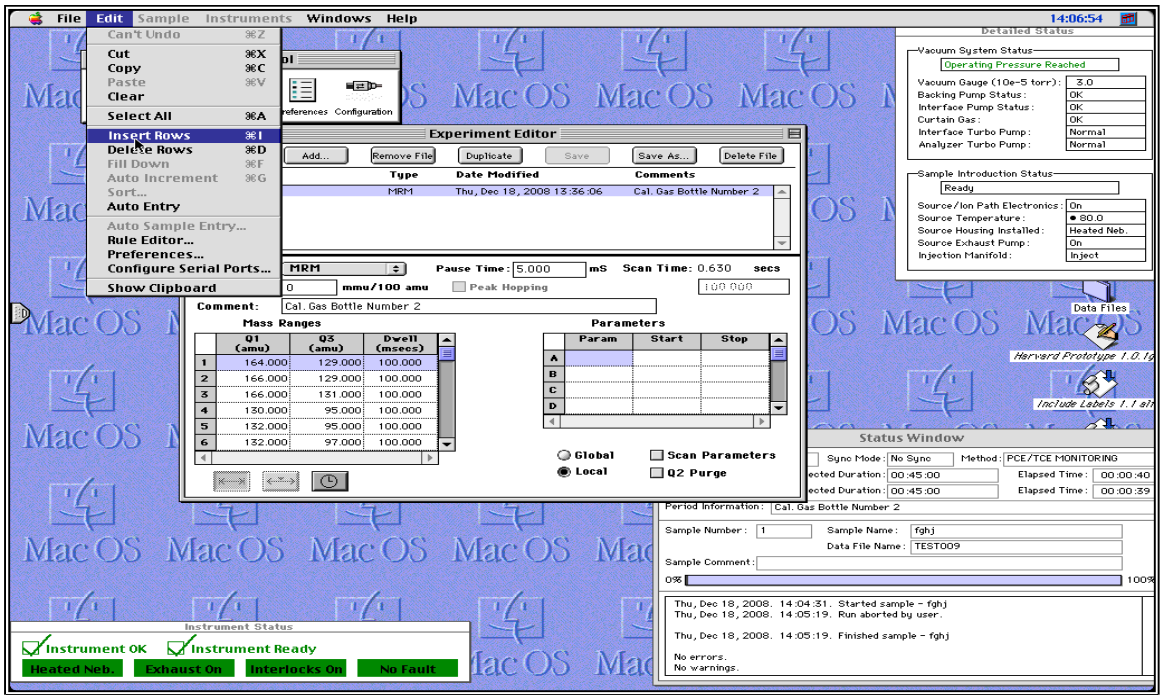

Figure 7.11.6 Inserting Additional Rows in Experiment

15) At the menu bar, click [EDIT] → [Insert Rows]. This will insert a blank row above the line selected. This can be repeated as often as necessary. To date experiments using up to 34 ion pairs have been created,
16) Save the Experiment. **IMPORTANT: An Experiment created under SAMPLE CONTROL can be opened under TUNE, however, only the first eight ion pairs will be included. If you then click [SAVE] while in TUNE, all of the ion pairs after the first eight will be permanently lost.**
17) Changing Parameters for Different Ion Pairs.
    a. If the Experiment includes ion pairs from differing types of compounds, and the optimum tune conditions for those compounds (or different ion pairs of the same compound) are significantly different, optimum response from all of the ion pairs may often be achieved by using different parameters for each of the ion pairs. This must be done with caution because changing parameters can change resolution for the ion pair. **In general, changing only RO2 for the different ion pairs may be sufficient** (Figure 7.11.7)

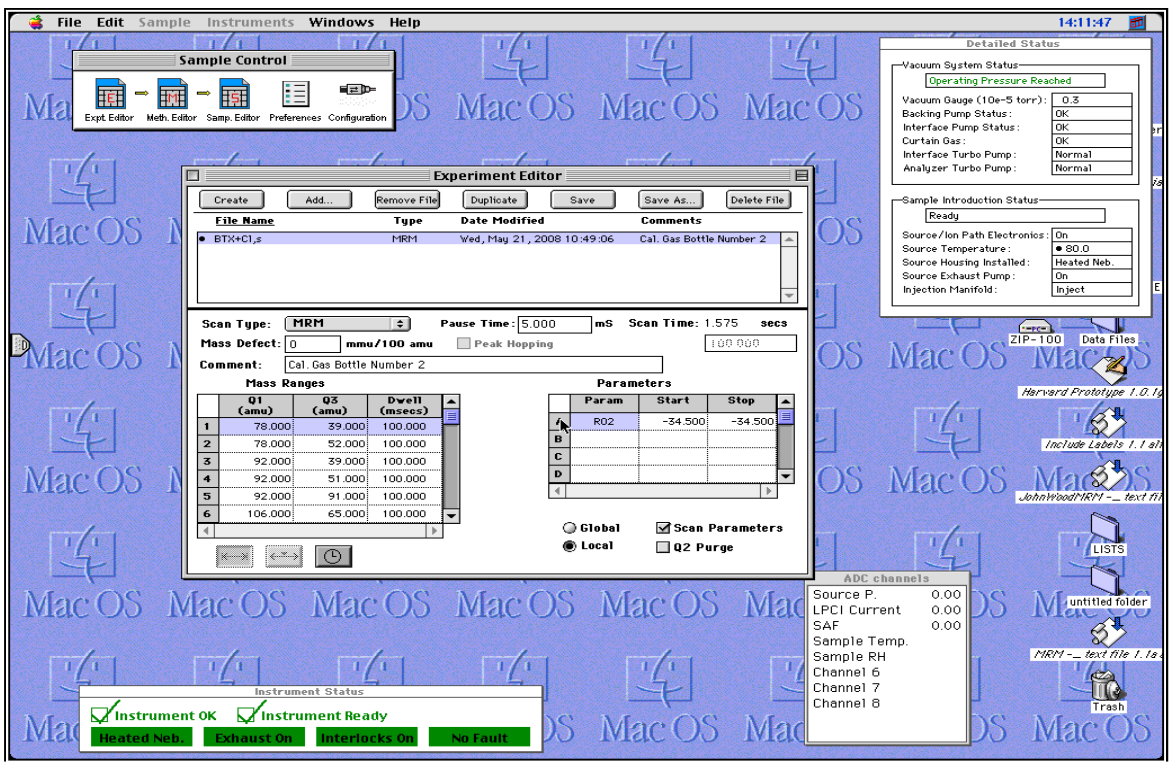

Figure 7.11.7 Entering Different Parameters for Ion Pairs

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    b. The parameters and their corresponding values would have been determined in Tune prior to the creation of the Experiment.
    c. In the "Mass Ranges" section, click on any cell in the row containing the ion pair requiring parameters different from those specified by the State File. The "Parameters" section will then become available for entries.

d. Click in the 'Param' cell next to the letter "A". Select the required parameter from the drop down menu (usually RO2).
e. Using the "Tab" key to move right, enter the necessary value in both the Start and Stop columns (we do not scan the value during the dwell time). **Caution: be sure to include the correct polarity for the voltage. The software is very literal, and entering 37 when -37 should have been entered will result in zero ion intensity for that ion pair.**
f. Additional specific parameters can be added for that ion pair by entering them in the other lettered rows.
g. Repeat steps c through f for each ion pair requiring parameter modification.
h. When all parameter entries have been completed, check the Scan Parameter box below the Parameters section (Figure 7.11.7). This allows the Experiment file to override the State file values and use the values specified. Any parameters not specified in the Experiment file will default to the value in the State file associated with the Experiment by the Method.

18) Click [SAVE], make sure to be in the appropriate directory: US EPA (1 or 2)/Instrument/Experiment. Enter the desired file name, if not already entered, and click [SAVE].
19) Click the square box in the upper left corner of the Experiment Editor to exit the window.

7.12 Create Method Files Using Sample Control

The Method File is used by TAGA EXPRESS to run the instrument. The Method file includes the Experiment file, the Q1 and Q3 Calibrations, and the State file to be used during analysis, and will include the length of the analysis.

7.12.1 Creating a Monitoring Method

1) In the Sample Control pane, double click on the Method Editor icon to open (Figure 7.11.8).

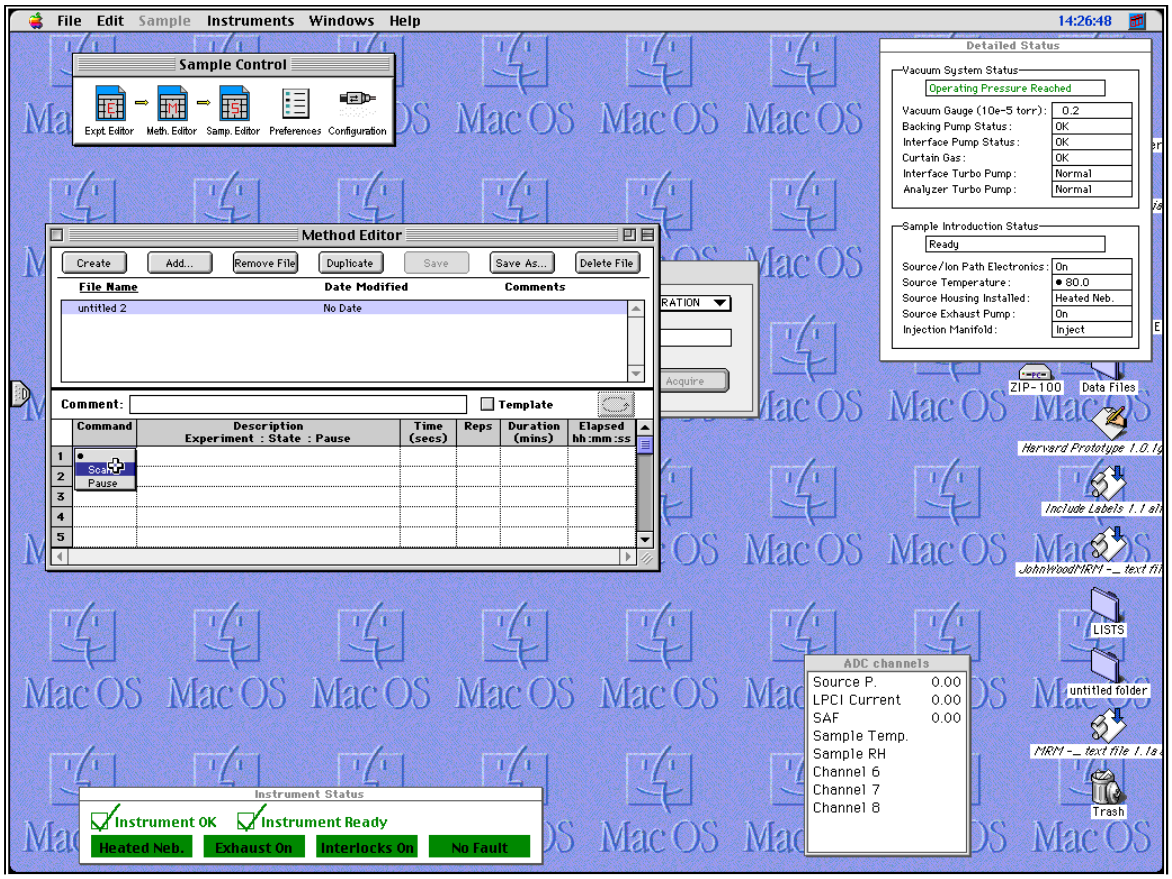


Figure 7.12.1 Creating a New Method File

2) Click [CREATE]. Double Click on the highlighted box in row 1 (Figure 7.12.1). Click on “Scan”.

3) Double click in the adjacent box under Description. Enter the appropriate Experiment file name, State file name, Q1, Q3 and Threshold. (Figure 7.12.2)

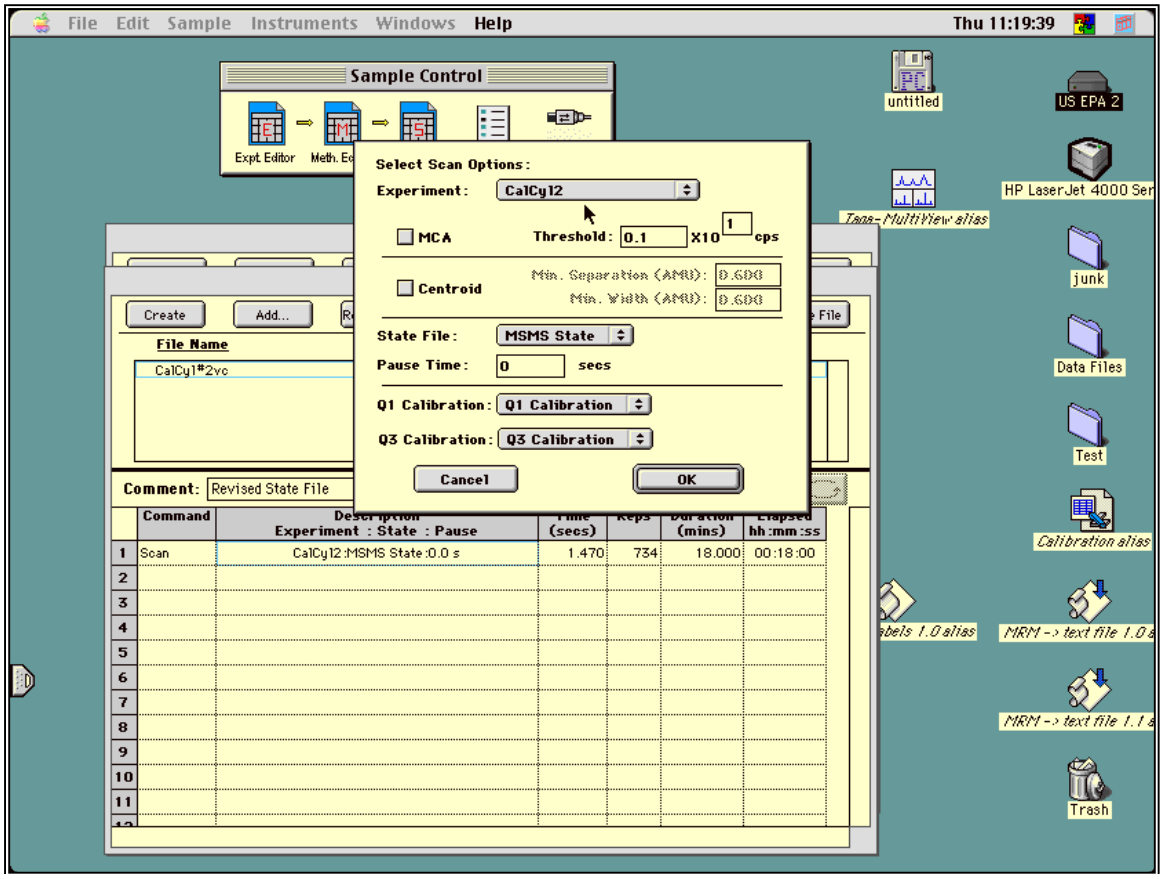


Figure 7.12.2 Entering Experiment file and State File

4) Double click on the same line in the box under "Duration", and enter the number of minutes you want the run to last. Note that the duration listed in the Experiment file is not used when running a Method.
5) Click on Save As, and select a method name, including the word, 'monitoring' in the name.
6) Click 'File', 'Print' to print a copy of the method.

7.12.2 Creating a Calibration Method

1) The easiest way to create a calibration method associated with a specific monitoring method is to load the monitoring method, then click Save As, and replace the 'Monitoring' with 'Calibration' in the name. Then proceed to Step 3.
2) Follow steps 1 through 5 in 7.12.1, but substitute the word, 'calibration' for 'monitoring' in the method name.
3) In the command line, click 'Instruments', Select [PUMP], then [MKS 146 DOUBLE (or single)]. The mass flow controller program will be displayed (Figure 7.12.3). Flow A is MFC #1 and Flow B is MFC #2. Note that while the software indicates flows in ΦL per minute, the actual flow will be in mL per minute. This label cannot be changed by the user. **Note: Since the analog to digital converter was installed by ECA, the second MFC channel cannot be controlled by the computer.**

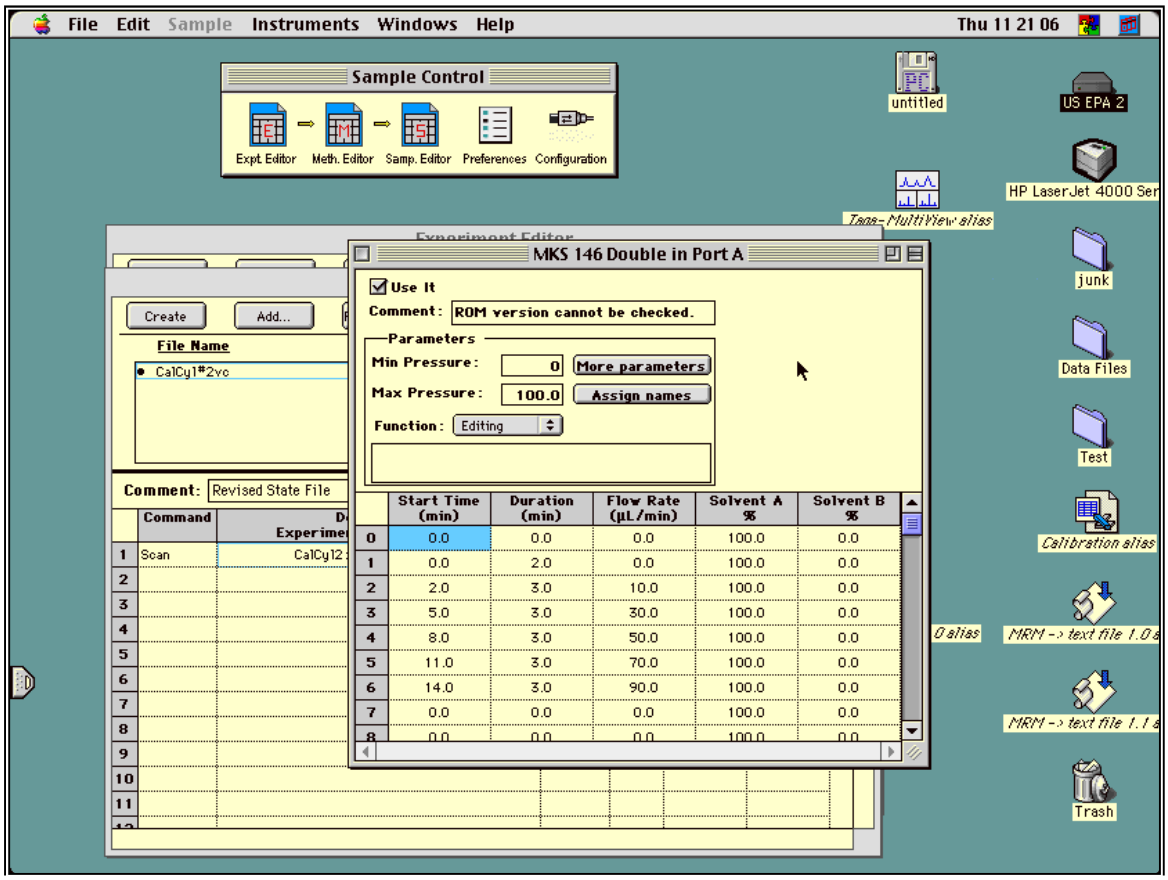


Figure 7.12.3 Mass Flow Controller Program

5) Make sure that the 'Use It' box is checked – this will enable the flow and time data to be entered.
6) Enter the duration and flow data for the calibration sequence. This is usually 2-minutes

at zero flow, then two minutes for each level, starting at 90 mL/min, then 10, 20, 40, 80, and 90 mL/min.

7) Close the pane.
8) Click, File, Save.
9) Select 'File', 'Print' to print a copy of the Method.

7.13 Background Subtraction

Background subtraction is used within Multiview to 'clean up' a file or to search for levels of specified substances that are buried below the noise level. This can be particularly useful when searching for parent or daughter ions within a mass spectrum containing significant background noise. It is most often used during method development, as demonstrated in the next section. The TAGA Multiview software provides background subtraction options which allow subtracting a single mass spectrum (or an average of the mass spectra in a time range) from another mass spectrum (or an average of the mass spectra in a time range), or to subtract the average background mass spectrum through a specified time range from every scan in the entire run.

7.13.1 Subtract Pane - Different Portions of the Same File

Subtract Pane is used to subtract the average of a selected time range within a run from another selected time range within the same run. This can be done with files generated using the Q1, Q3 or MRM modes of operation. Subtract Pane can be done with completed files or with individual spectra or ranges from files that are still being collected.

1) While in the Multiview screen displaying the total ion chromatogram, using the mouse, click and drag through a range for the area of interest (Figure 7.13.1).

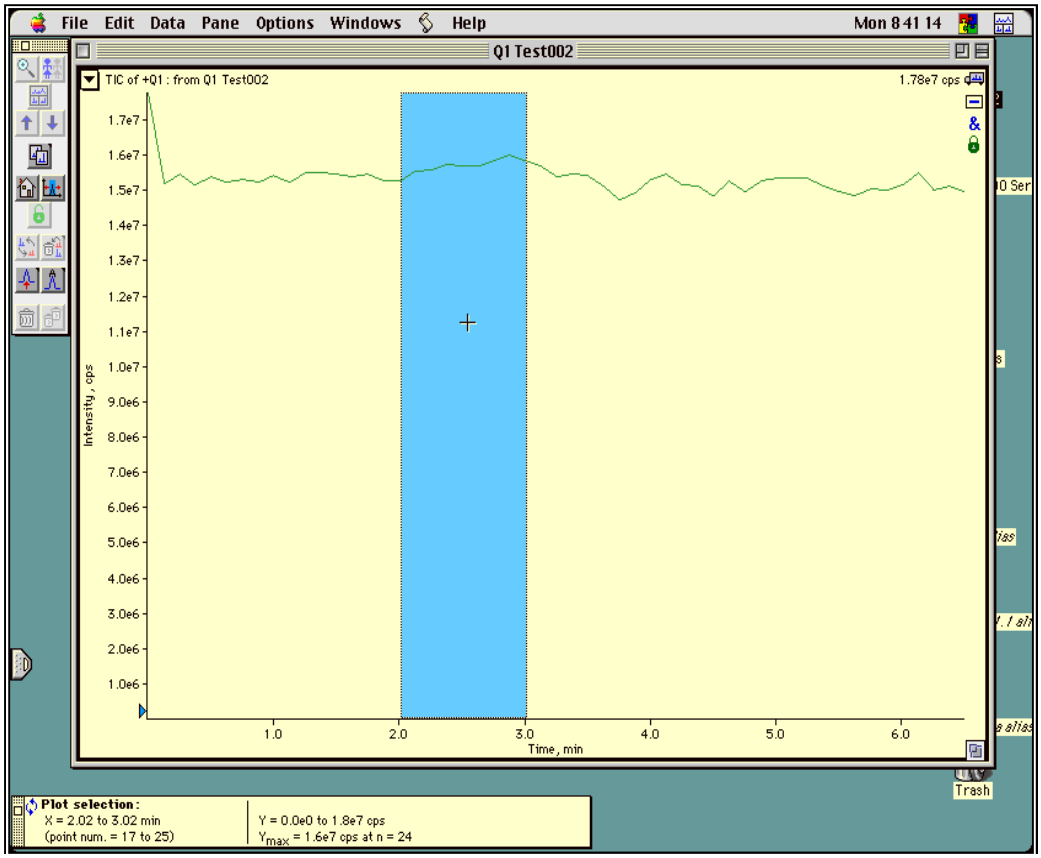


Figure 7.13.1 First Selected Area (Sample)

2) Place the cursor in the shaded, selected area, and then double click the mouse . This produces a separate pane containing the average mass spectrum for the selected area (Figure 7.13.2).

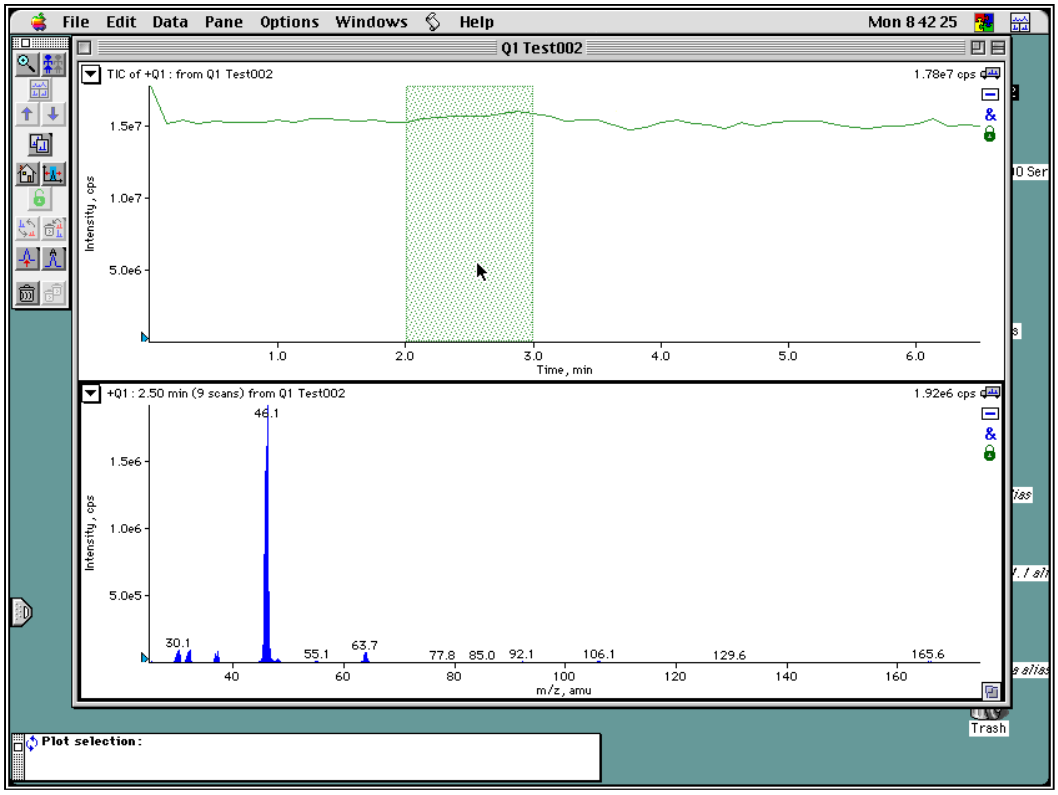


Figure 7.13.2 Average Spectrum in First Selected Area (Sample)This example consists of a Q1 scan in the LPCI mode of operation. A small amount (10 mL/min) of Standard Cylinder #2 was injected from two to three minutes during the run, producing concentrations of five to six ppbv of most of the compounds, with about 14 ppbv of xylene and 3.3 ppbv of vinyl chloride. The addition of the standard did not produce a significant effect on the baseline TIC trace.

In this Figure, the top pane presents the Q1 total ion chromatogram, with the shaded area of concern. The averaged mass spectrum of the area of concern is on the bottom. Note that the mass spectrum is dominated by cluster ions, and that the substances in the standard are not very noticeable.

3) Select the pane displaying the total ion chromatogram. Click and drag through a range for the background (Figure 7.13.3).

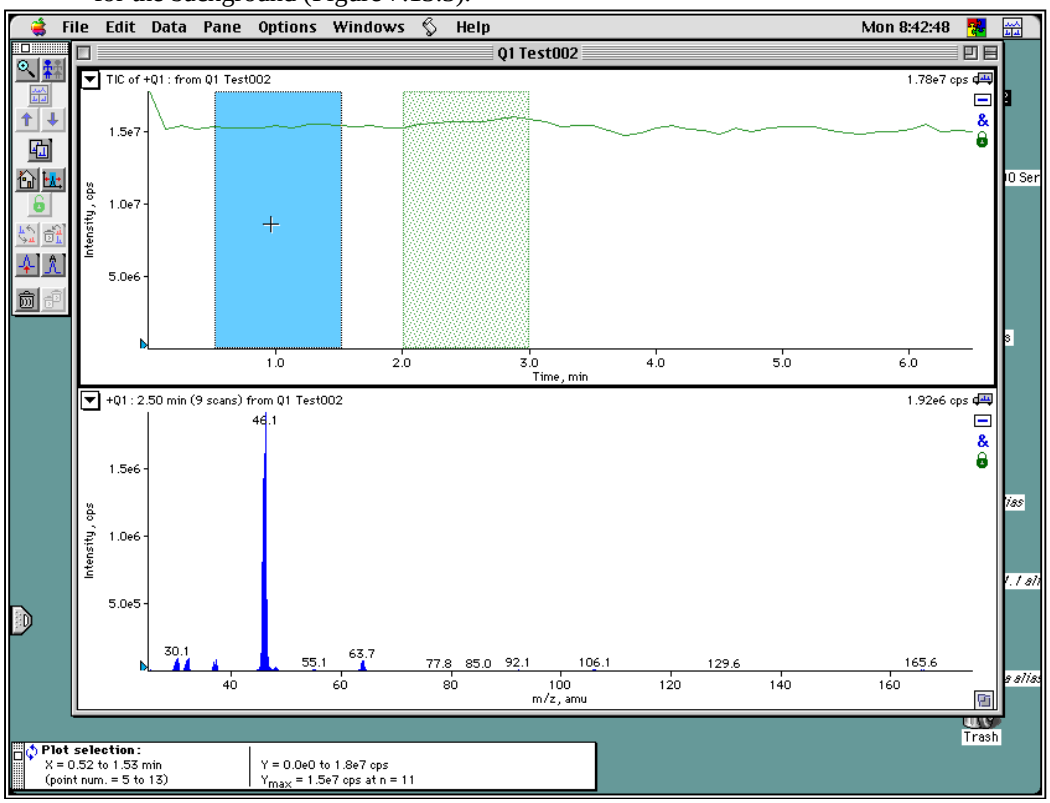


Figure 7.13.3 Selecting the Background Area

4) Place the cursor in the shaded, selected background area, and then double click the mouse. This produces a separate pane containing the average mass spectrum for the background area (Figure 7.13.4).

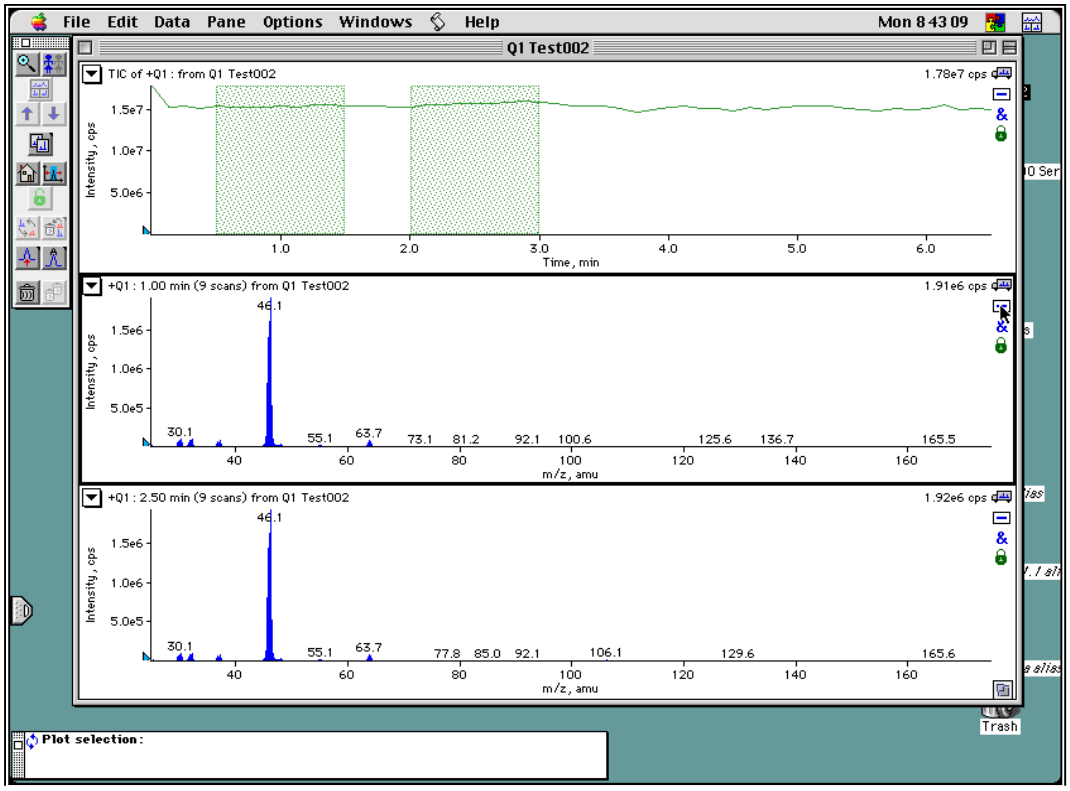


Figure 7.13.4 Average Mass Spectrum of Background Area Included

The average mass spectrum of each of each of the two selected areas is provided. Note that the run time of the center of each selected area is shown in the upper left portion of the pane containing the averaged mass spectrum.

5) Drag the Subtract Pane Icon (the minus sign in the upper right side of the active pane in the middle of the figure) from the background pane to the pane from which you want the background subtracted. This produces a background subtracted mass spectrum of the area of concern (Figure 7.13.5).

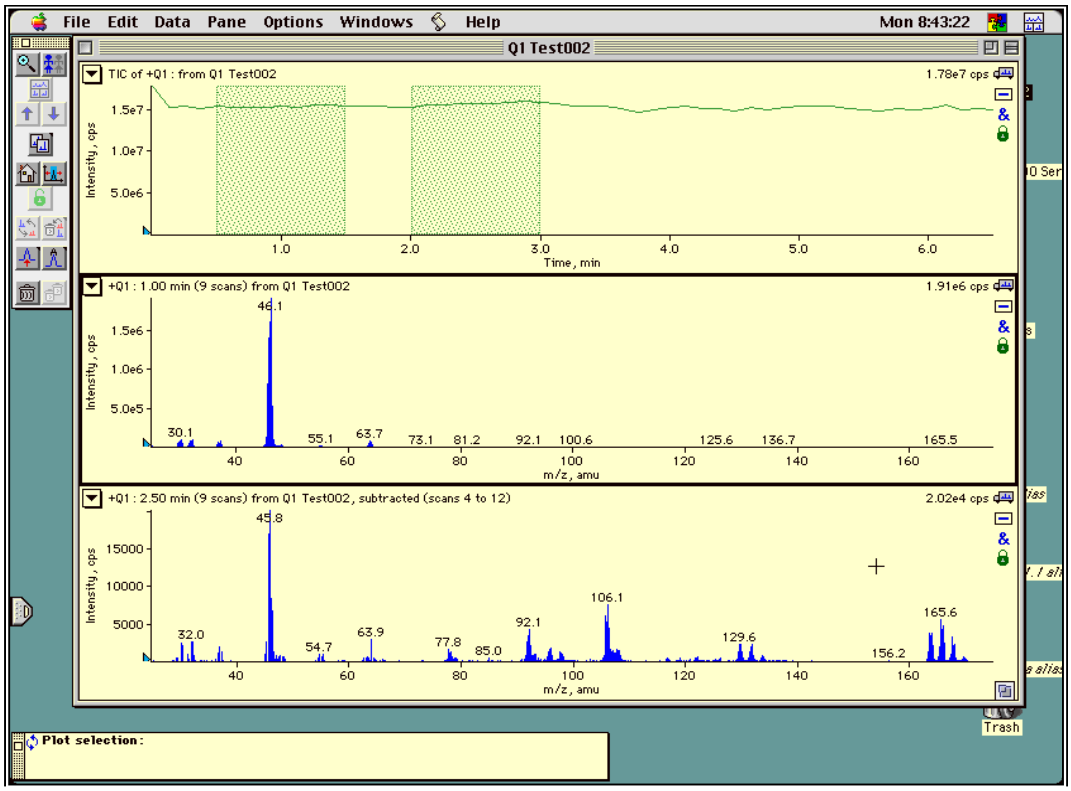


Figure 7.13.5 Background-Subtracted Q1 Mass Spectrum

The top two panes of this figure are identical to the ones in the previous figure. The bottom pane now shows the result of subtracting the middle pane from the bottom pane. The concentrations range from 3.3 to 6.7 ppb for most of the substances.

7.13.2 Subtract Pane - Average Spectra of Portions of Different Files

Subtract Pane is used to subtract the average of a selected time range within one file from another selected time range within another file. This is usually done with files generated using the Q1 mode of operation.

1) While in the Multiview screen displaying the total ion chromatogram of the file to be used as background, click and drag through a range for the area of interest (Figure 7.13.6).

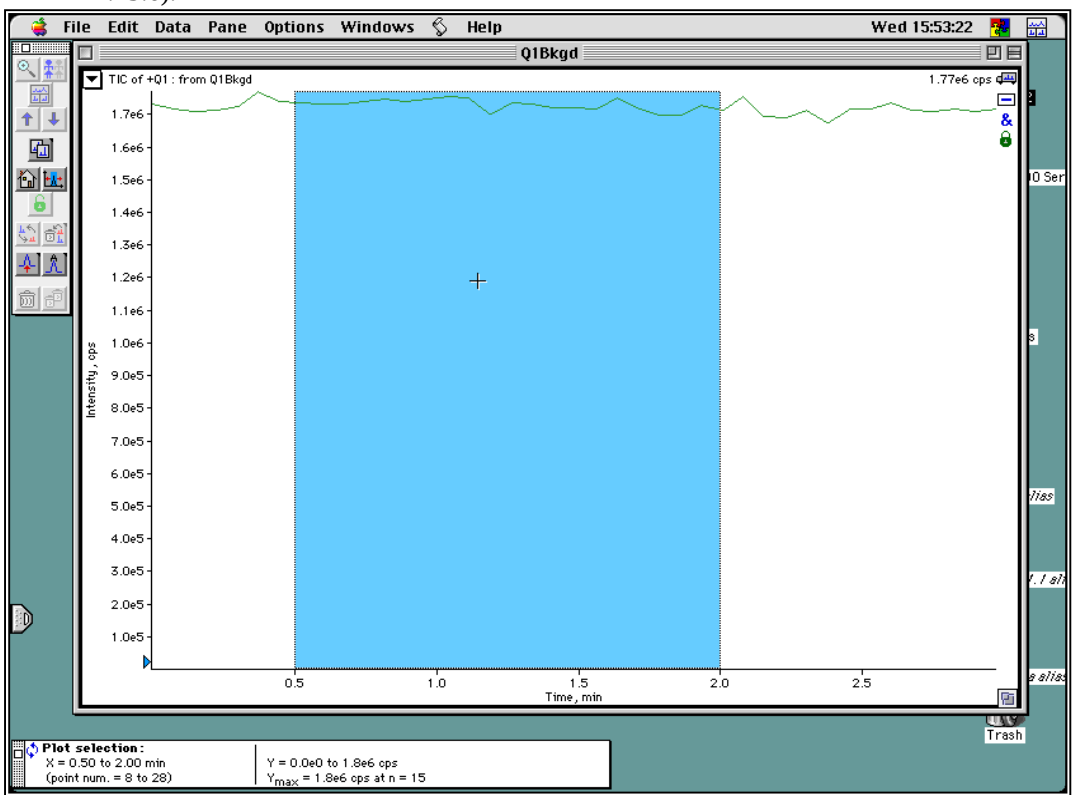


Figure 7.13.6 Selection of Background from First File

2) Place the cursor in the shaded, selected area, and then double click the mouse. This produces a separate pane containing the average mass spectrum for the selected area (Figure 7.13.7).

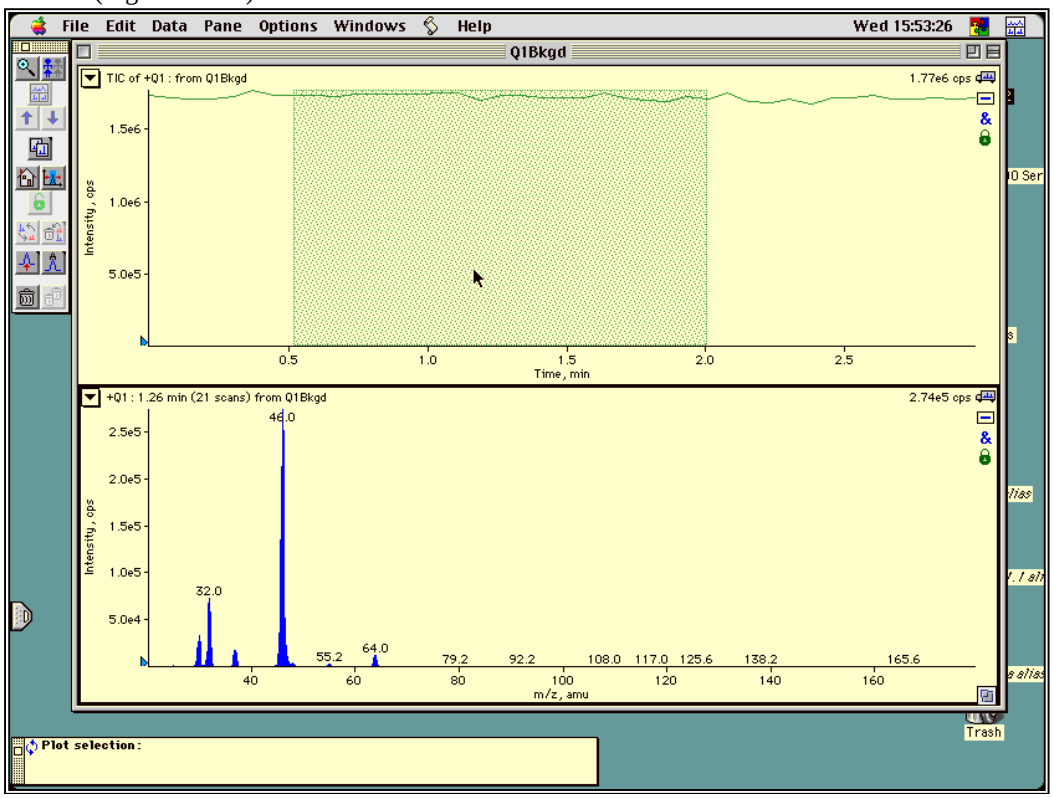


Figure 7.13.7 Display of Averaged Background Spectrum from First File

3) While in the Multiview screen displaying the total ion chromatogram of the file from which the background is to be subtracted, click and drag through a range for the area of interest (Figure 7.13.8).

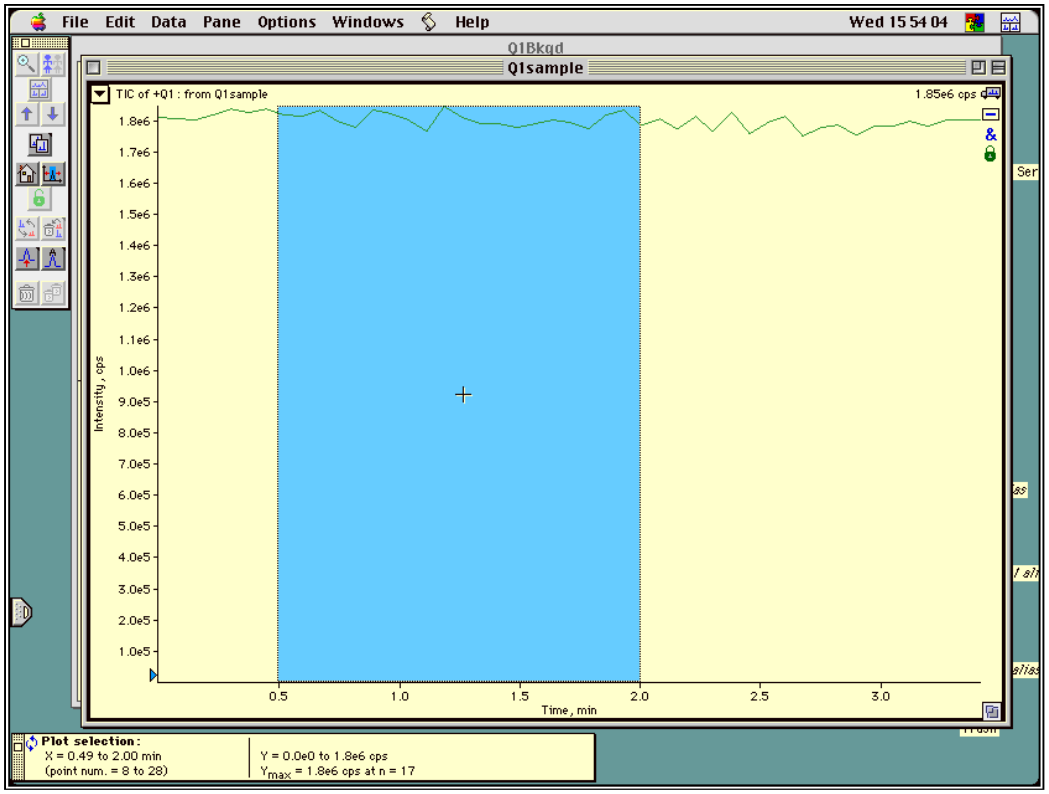


Figure 7.13.8 Selection of Area of Interest in Second File

4) Place the cursor in the shaded, selected area, and then double click the mouse. This produces a separate pane containing the average mass spectrum for the selected area (Figure 7.13.9).

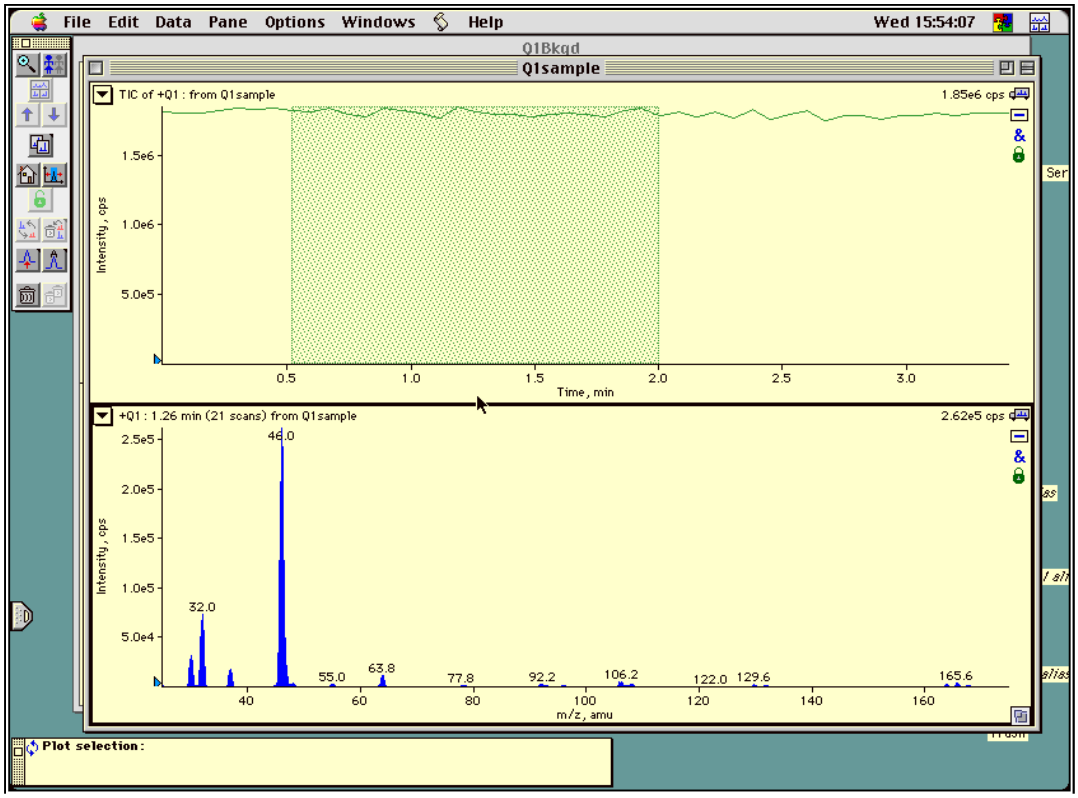


Figure 7.13.9 Display of Averaged Spectrum of Area of Interest in Second File

5) Make the Background Pane smaller, so you can access both files (Figure 7.13.10).

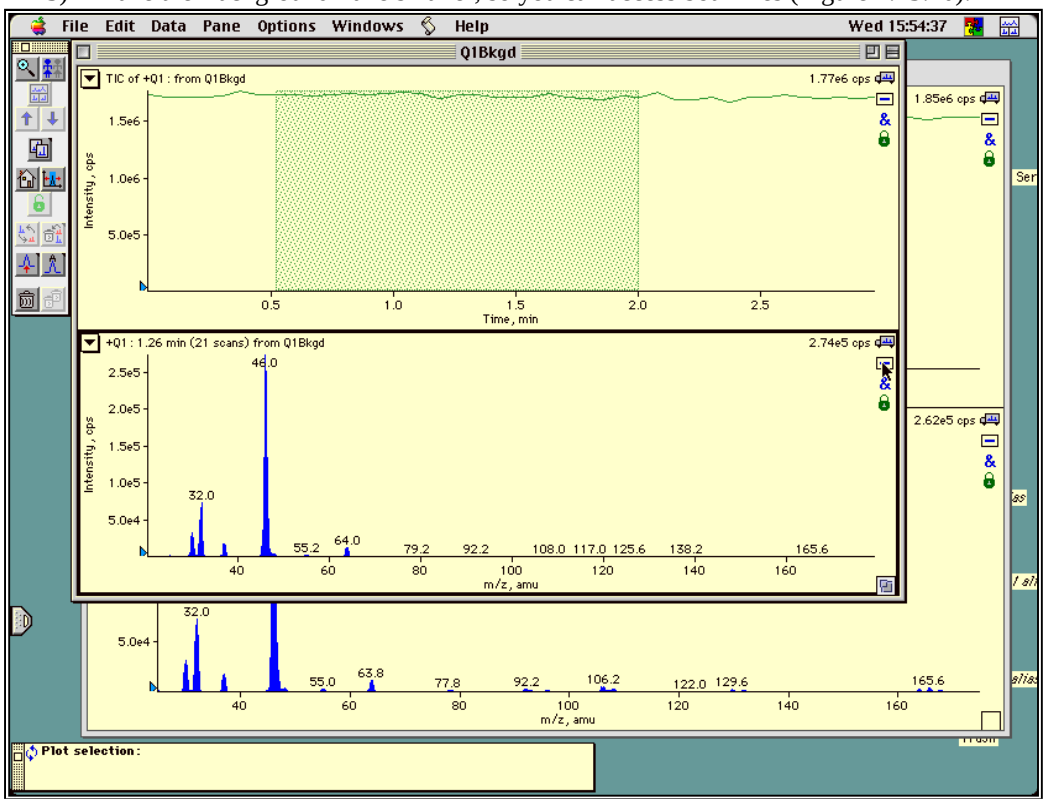


Figure 7.13.10 Decreasing Size of Background Pane

6) Drag the Subtract Pane Icon (the minus sign in the upper right side of the active pane in the middle of the figure) from the background pane to the pane from which you want the background subtracted. This produces a background subtracted mass spectrum of the area of concern (Figure 7.13.11).

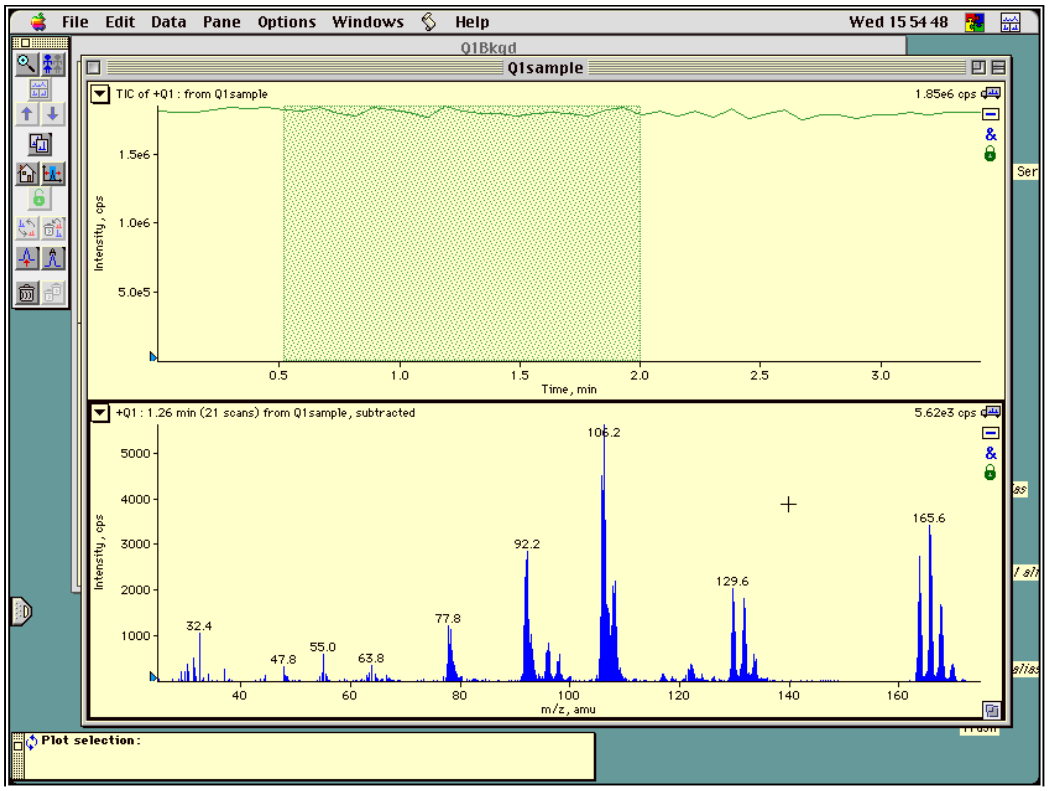


Figure 7.13.11 Background Subtracted Spectrum

This shows the result of subtracting the averaged background from one file from the target area of another file. In this case there are multiple substances present. The most common application for this function will be to determine the parent ions for a cylinder standard containing only the target substance and nitrogen.

7.13.3 Subtract to File

The "Subtract to File" command is used to subtract the average of a range of scans within a run from all of the scans within that run, and to save the background-subtracted files as a separate file. This can only be done with a completed file.

1) Using the cursor, select a background range within the run (Figure 7.13.12).

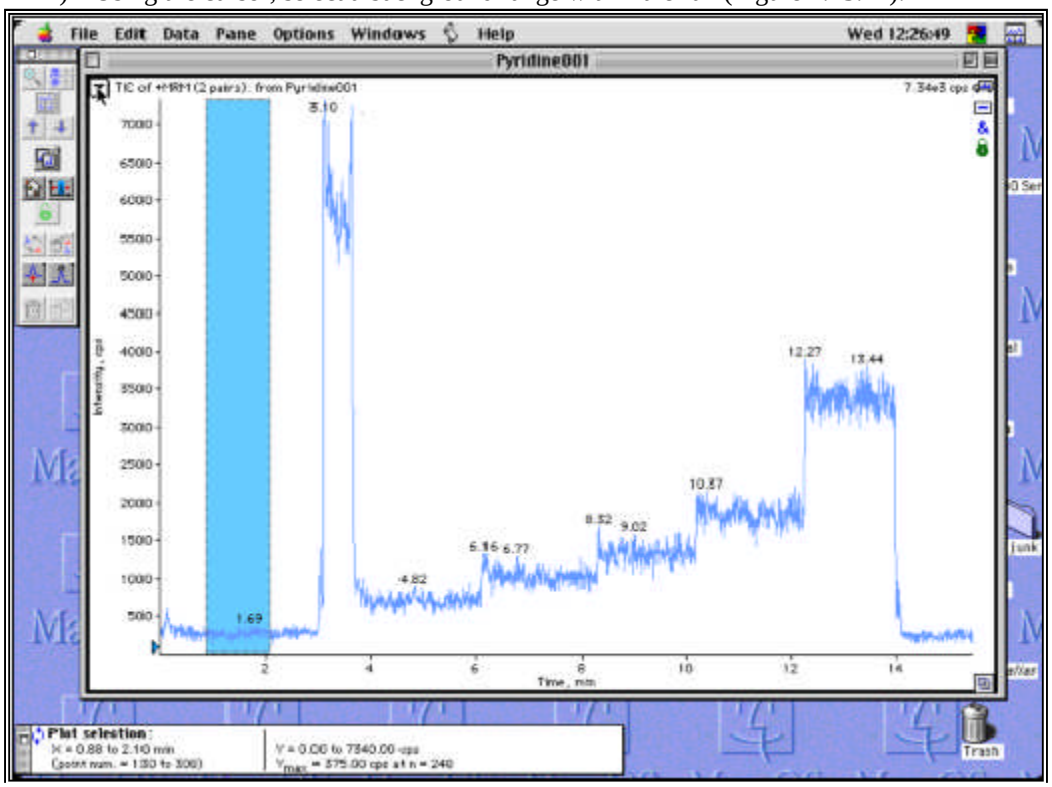


Figure 7.13.12 Selecting Background Range

The figure above shows a pyridine calibration run. In this example, a 10 µl syringe was filled with iso-octane, containing 10 ppmv of pyridine. The initial baseline was produced without the needle in the air stream (1500 mL/sec). The needle was then inserted and the syringe pump set at a relatively high flow rate in order to get the liquid to the needle tip, thereby, producing a high spike. The syringe pump was then slowed to produce a pyridine concentration of 7.07 pptv from four to six minutes into the run.

2) Click on the Pane Command Pop-up Menu and select [SET SUBTRACTION RANGE] (Figure 7.13.13).

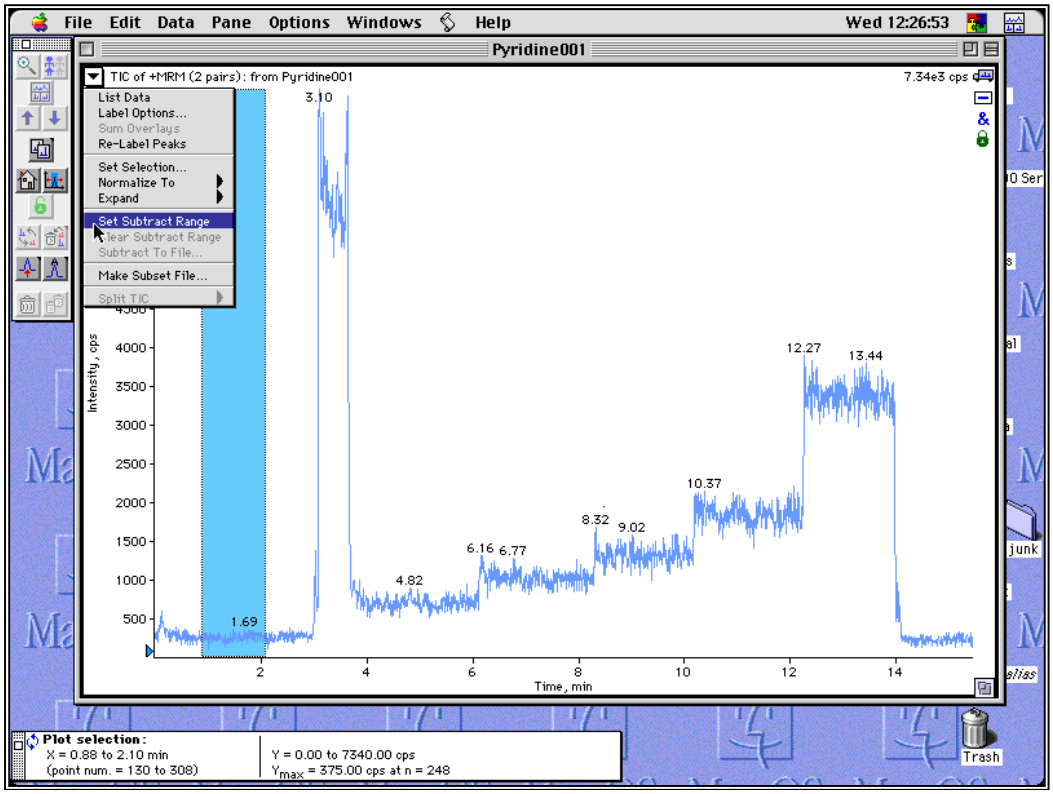


Figure 7.13.13 Set Subtract Range

The result of that action is shown in the next figure (Figure 7.13.14).

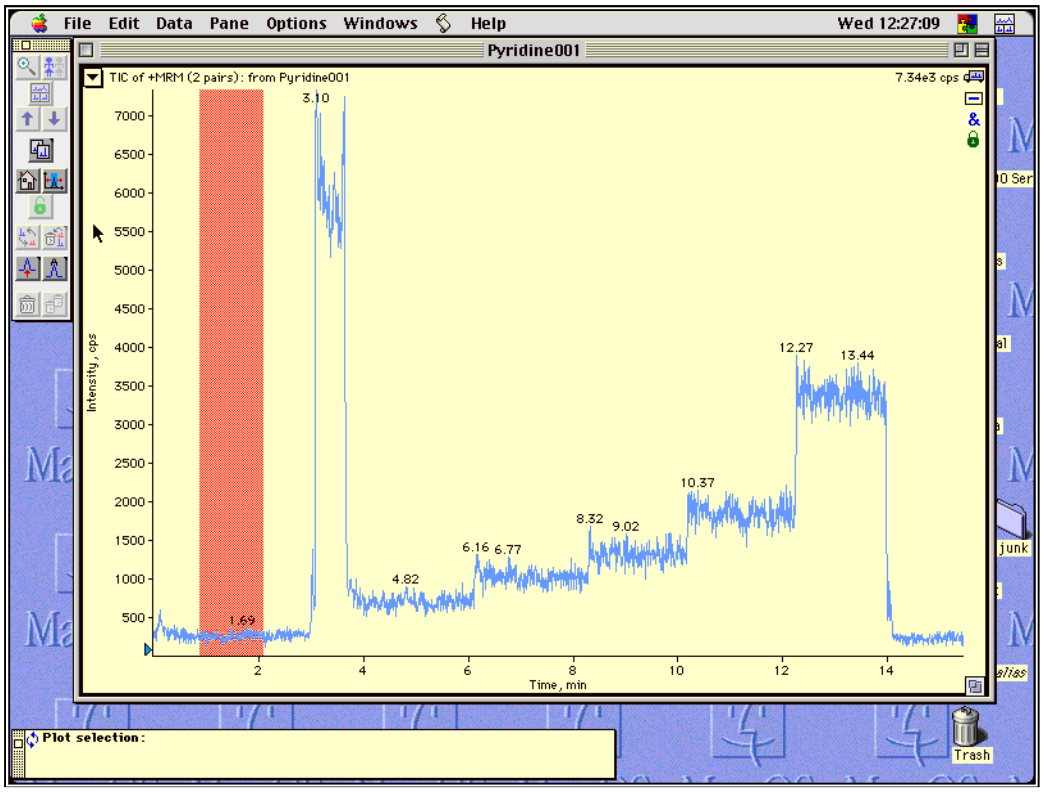


Figure 7.13.14 Selected Background for Subtraction

4) Select [SUBTRACT TO FILE] from the pop-up menu. A dialog box comes up, requesting a file name and file location (Figure 7.13.15).

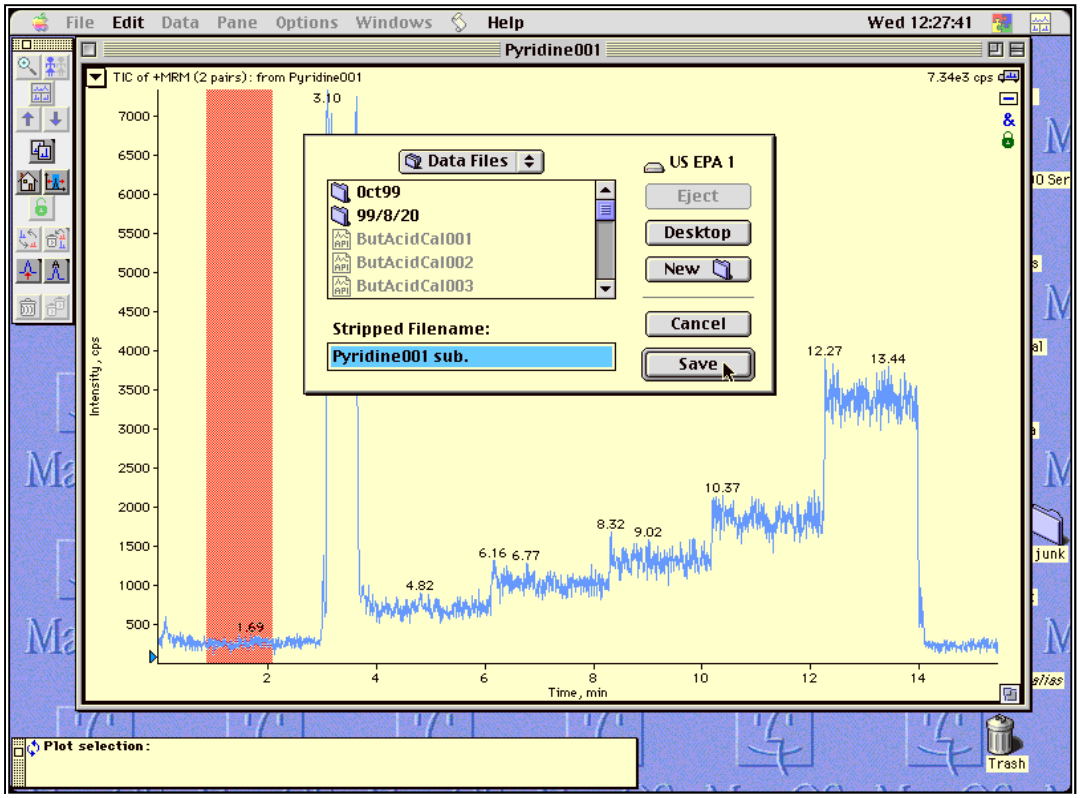


Figure 7.13.15 File Selection for Subtracted File

7.14 Method Development

Normally, the first step in developing a TAGA method for a target substance is to run a Q1 scan using the appropriate inlet and mode. The basic modes are LPCI (positive and negative) and APCI (positive and negative). The chemist will use previous experience, knowledge of source chemistry, and the likely matrix and sampling program to select the primary mode of operation. While they are presented separately below, the chemist will likely optimize the inlet and tuning conditions for the specific compound of interest while doing the basic Q1 work, then refine the inlet and tuning conditions as the Q3 and ion pair selection process proceeds.

7.14.1 Parent/Daughter Ions

Once the instrument has been set up in accordance with the chemist's expectations, the next step is to evaluate potential parent ions, also called precursor. After the parent ions are selected, the daughter ions (product ions) are selected.

1) Select [TUNE].
2) Select [STATE], [Q1 SCAN].

3) Select [LOAD EXPERIMENT], [Q1 SCAN].
4) Set the expected mass range to be appropriate for the target substance. If the range includes masses below 48 for the LPCI mode, the background intensity may be so great that you will need to use background subtraction to even see the ions associated with the target compound.
5) Set step size to 0.2 to 0.5 amu.
6) Set dwell time to 5 msec.
7) Select [SCAN], [START]. The instrument will start scanning in Q1 mode.
8) Select [DISPLAY], [AUTORANGE].
9) Select [DISPLAY], [REFRESH].
10) Print the display. This records the instrument background.
11) Introduce a small amount of the pure substance's vapor into the inlet. It is very important to start out with very small amounts to avoid problems with overloading the source and detector, and to minimize contamination of the inlet system.
12) Observe and print the scan. If no peaks have been added to background, either increase the amount of target substance or do background subtraction, as appropriate.
13) Evaluate the mass spectrum, paying particular attention to the location of the expected molecular ion (usually M or M+1 in positive ion mode, and M-1 in negative), the expected fragmentation pattern, and cluster peaks.
14) Based on the chemist's experience, source modes, and polarity of operation, the source parameters (see Figure 7.14.2) will vary to select conditions producing a combination of good sensitivity with acceptable fragmentation and minimal cluster peaks.
15) Print the mass spectrum once the optimum conditions are selected. The state parameters will be printed along with the mass spectrum.
16) Select [SCAN], [FINISH].
17) While there may be sufficient information to select the parent peaks at this point, it is advisable to do background subtraction and save the selection file to assure and document the correct selections.
18) Shut off the standard, so the initial scans in the subsequent run will be background.

19) Select [SCAN], [ACQUIRE TO DISK] (Figure 7.14.1).

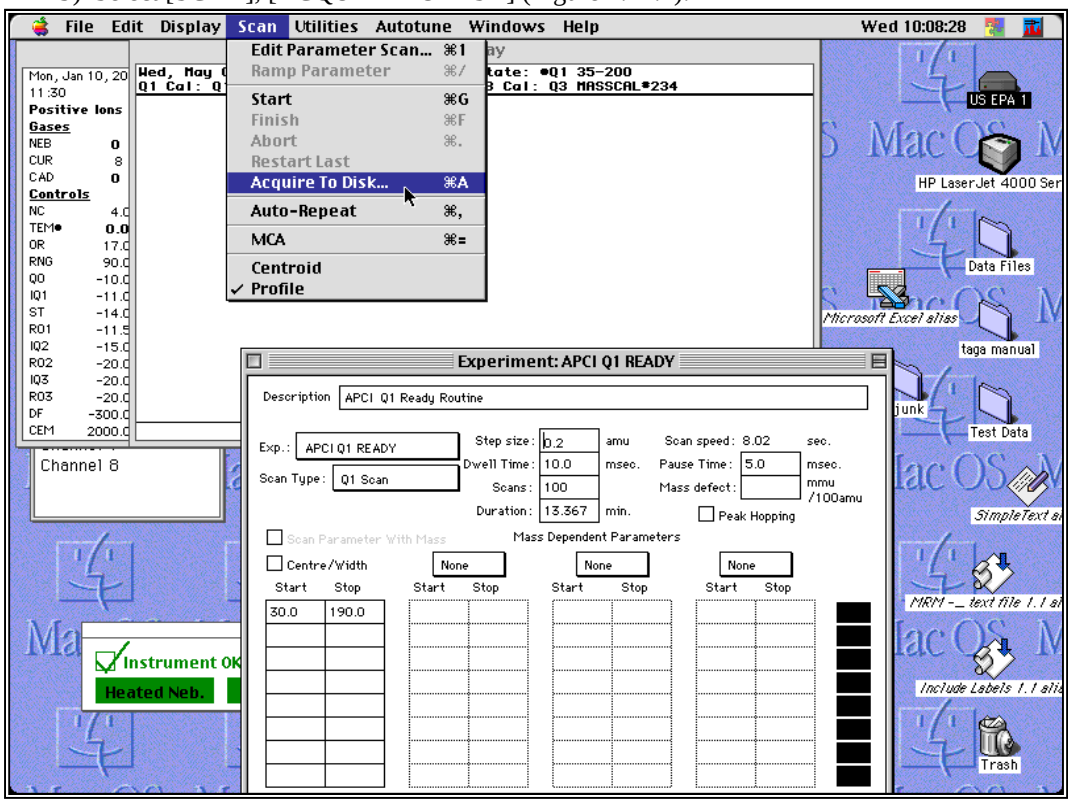


Figure 7.14.1 Acquire to Disk

It is most convenient to run the data collection and background subtraction for determining parent and daughter ions while in the Tune mode. It can be done from the Sample Control mode, but takes much longer to set up.

20) Since this is likely to become a permanent record, use a step size of 0.1 or 0.2 amu to provide better resolution.

21) A dialog box will appear, in which you can select the file name, directory, and threshold level (Figure 7.14.2). Store the file(s) in a folder named for the compound, and under the EPA 1 (or 2): Data Files: Parent/Daughter path.

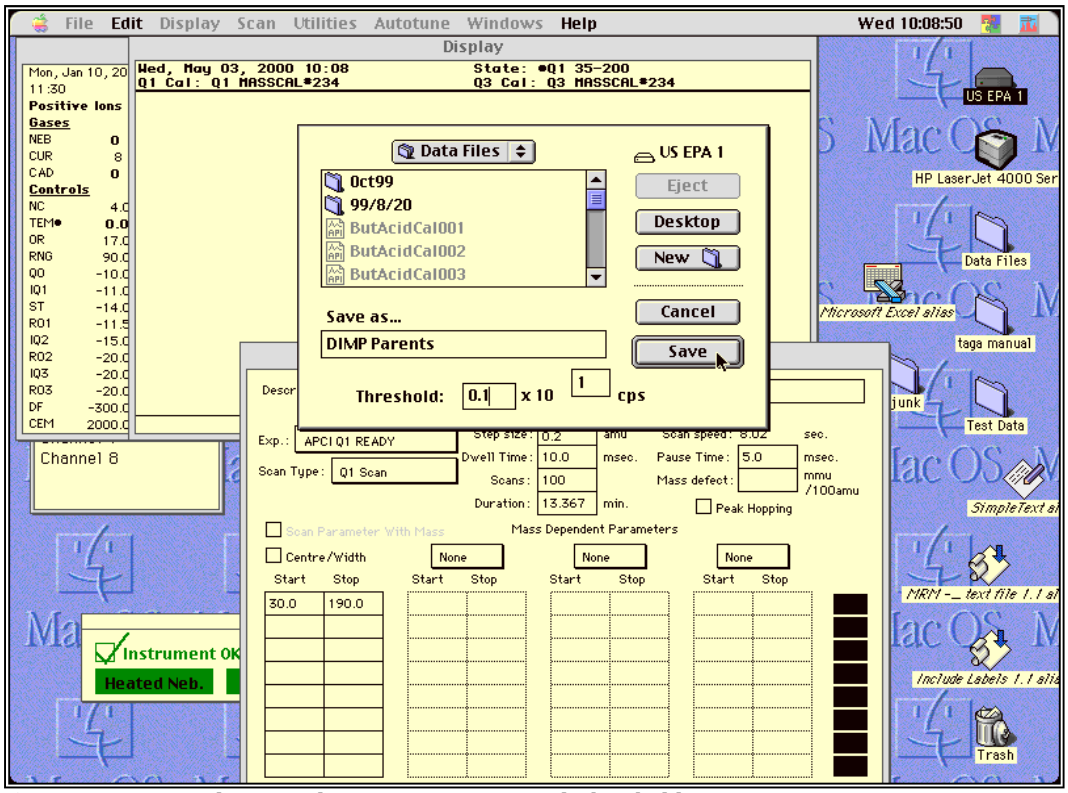


Figure 7.14.2 Selecting File Name, Directory and Threshold

22) When you have completed filling out the dialog box, select [SAVE]. This starts data acquisition and saves the data to the file.
23) As soon as data acquisition starts, it will display the TIC automatically. To see the mass spectra, use [DISPLAY], [MASS SPECTRUM].
24) After you have collected at least ten background mass spectra, turn on the MFC or syringe pump to introduce standard to the TAGA.
25) When you have collected at least ten complete mass spectra of the standard, end data collection by selecting [SCAN], [FINISH].

26) Select [Apple], [MULTIVIEW].
27) Select [FILE], and then double click the file name.
28) The total ion chromatogram will be displayed.
29) Click and drag through the selected background region, then double click inside the highlighted area (Figure 7.14.3).

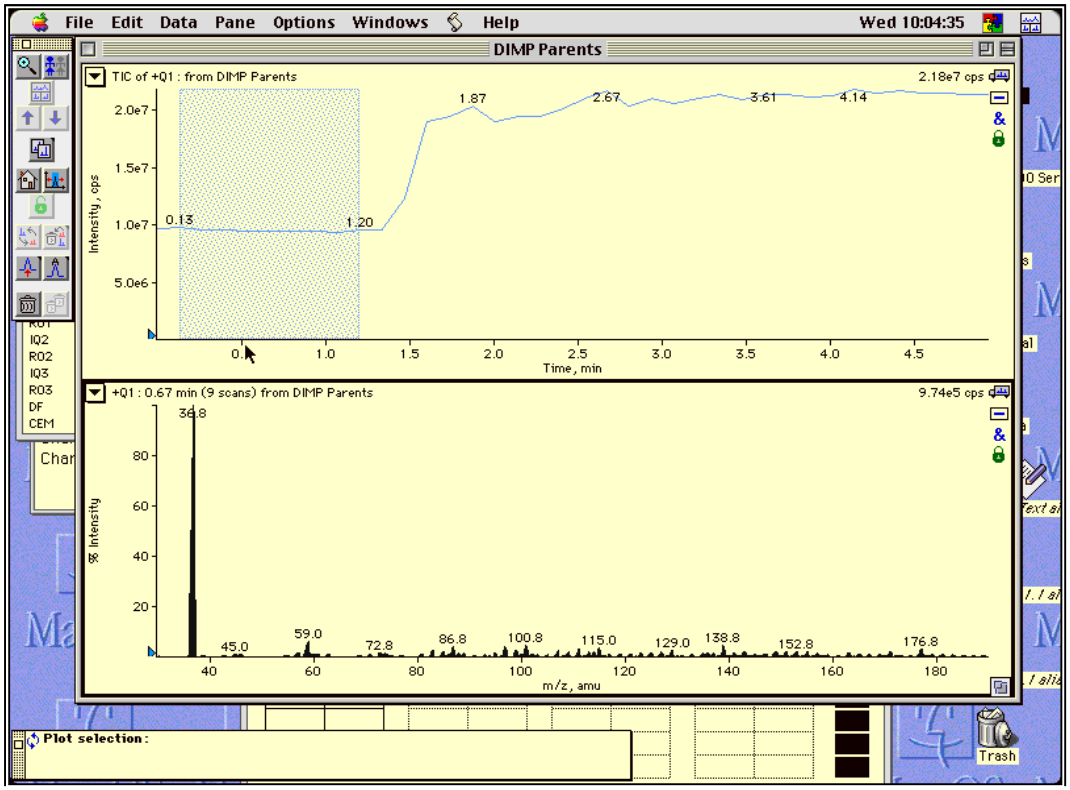


Figure 7.14.3 Selecting the Background

30) The average mass spectrum of the background region will be displayed in the lower pane.

31) Click and drag through a sample region with approximately the same collection time span, and double click inside the highlighted area (Figure 7.14.4).

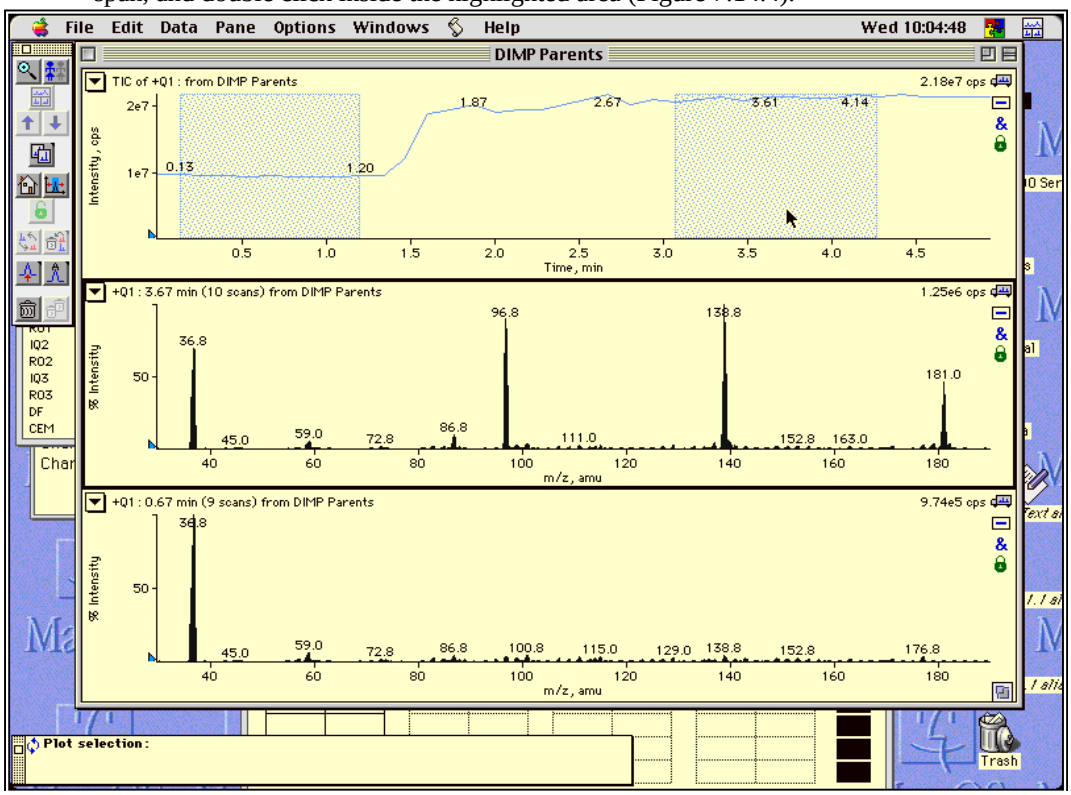


Figure 7.14.4 Mass Spectrum of Sample Region

The bottom pane of this figure presents the average mass spectrum of the background centered on 0.67 minutes. The middle pane presents the average mass spectrum of the region centered on 3.67 minutes, during the injection of the DIMP standard. The next step is to subtract the background mass spectrum from the mass spectrum containing the standard.

32) The averaged mass spectrum of the sample area will be placed in the middle of the display as shown in the figure above.
33) Click and drag the [-] in the upper right portion of the background (lower) pane into the sample (middle) pane. When you release the mouse button, the background-subtracted mass spectrum will be displayed in the middle pane (Figure 7.14.5).

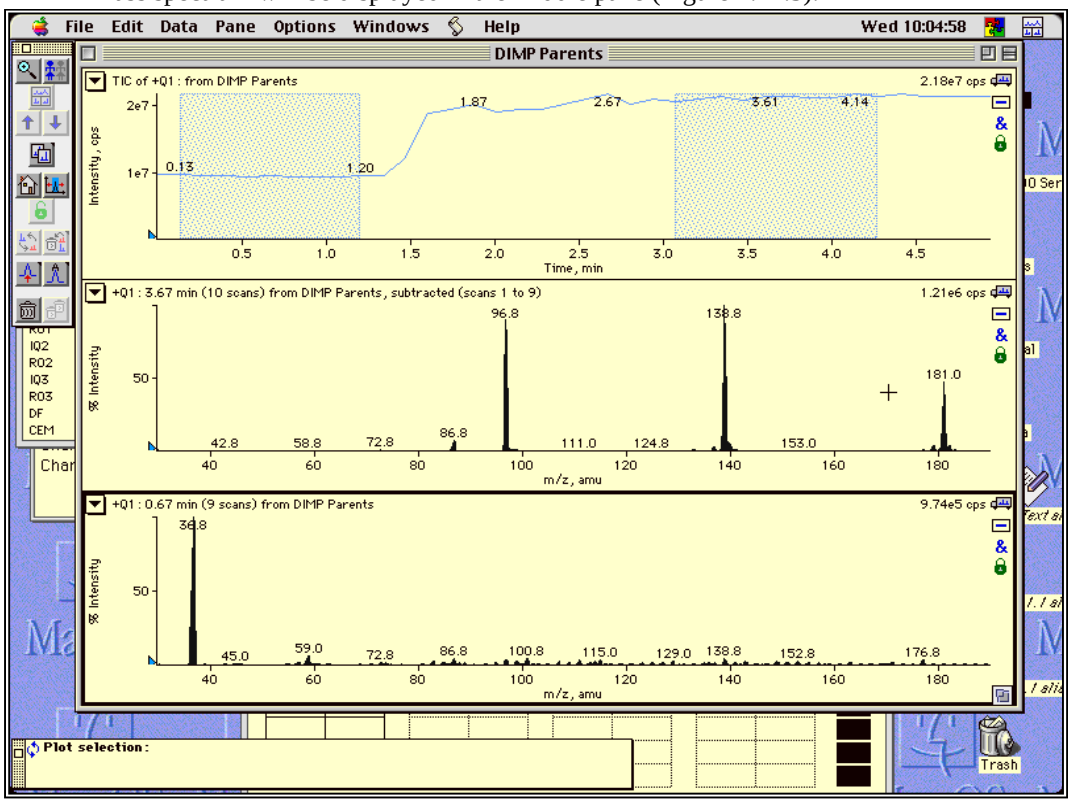


Figure 7.14.5 Background-Subtracted Parent Ion Mass Spectrum

The center pane contains the background-subtracted parent ion mass spectrum. The three primary parent peaks are 181, 139, and 97 amu. Note that the molecular weight of DIMP is 180 amu, but the 'molecular ion' is really M+1, or 181 amu. The small peak at 87 amu was found to be due to contamination in the mass flow controller. This peak would have been avoided in the final mass spectrum if the background mass spectra had been collected while passing nitrogen through the mass flow controller at the same rate as later used for the standard.

34) Select the parent ions to be used for further analysis. In the case of the example, 181, 139, and 97 amu.
35) Click on the box in the upper right corner of the screen, and select [TUNE].
36) Select [FILE], [OPEN STATE FILE], and select an appropriate MS/MS STATE file.

37) If necessary, modify (and save to an appropriate name) the top four Controls to agree with those selected during optimization of Q1. This is most likely to be necessary when operating in the APCI mode.
38) Select [FILE], [OPEN EXPERIMENT FILE], [DAUGHTER SCAN].
39) Enter the first parent mass, and enter a scan range that is appropriate for that parent ion.
40) Acquire the scan to file and do the background subtraction as shown above (an example background-subtracted daughter mass spectrum is shown in Figure 7.14.6).

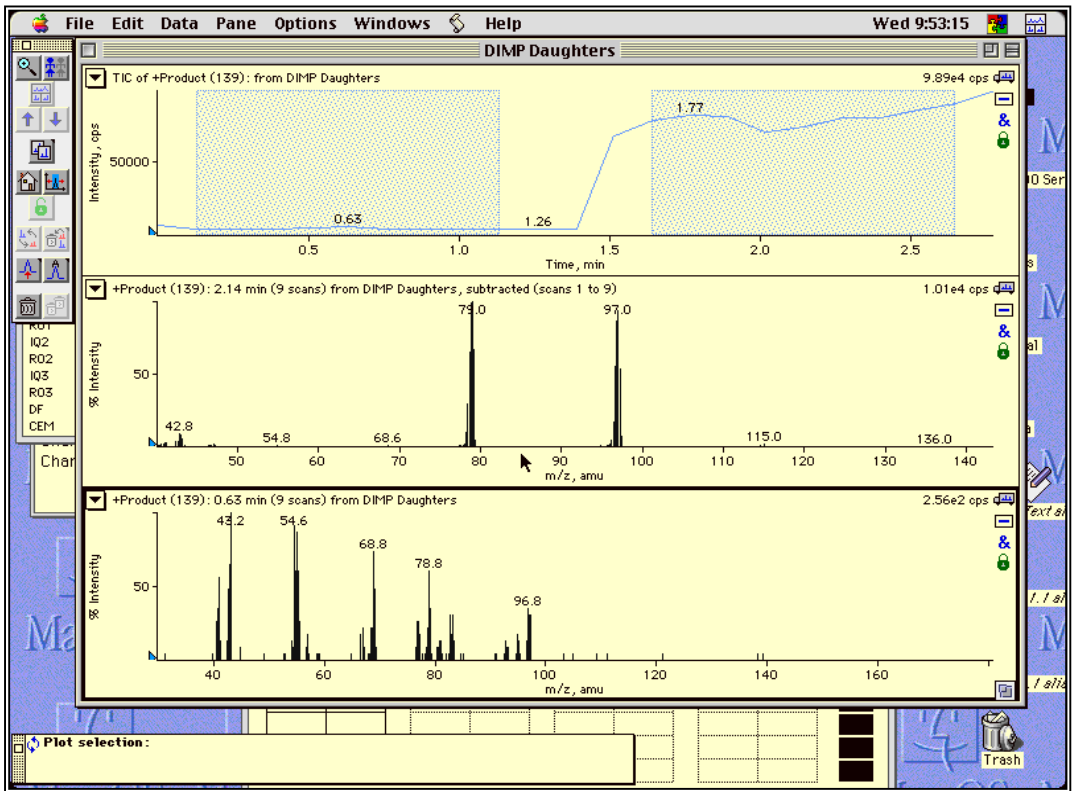


Figure 7.14.6 Background-Subtracted Daughter Mass Spectrum

The middle pane shows the background-subtracted daughter mass spectrum of the 139 amu parent ion. Note that both the 79 amu and 97 amu daughters have similar intensities and are both good candidates for quantitative use.

41) Once the process is repeated for all of the selected parent ions, the appropriate candidate parent/daughter pairs can be selected.
42) Select [LOAD EXPERIMENT FILE], [DEVELOP].
43) Enter the selected parent/daughter ion pairs (up to eight pairs) into the appropriate boxes on the screen. Set dwell to 100 ms for each pair.
44) Select [SCAN], [RUN]. A real time chromatogram for all of the ion pairs will be produced.
45) Vary the concentration of the target substance during the run, and note whether or not the candidate ion pairs respond in proportion to the varying target substance concentration.

46) Eliminate any ion pairs that do not respond in proportion to the varying concentration.
47) The remaining ion pairs are the new candidate ion pairs.
48) Review the masses of the parent and daughter ions, and identify the probable structures of those ions.
49) Accept those ion pairs that, in the judgment of the chemist, are justified as being the result of the expected reactions and rearrangements for the target substance exposed to the selected source.

7.15 Changing Ionization Sources

Changing ionization sources requires about an hour. However, due to significant differences between the sources, extensive retuning may be needed prior to being ready to operate.

7.15.1 Removal of the LPCI Source

1) Turn off the electrode current, the TAGA and all of the rough pumps, including the rough pump attached to the source pressure controller. The latter is turned off by unplugging the yellow plug in the outlet behind the MKS Controller.
2) Turn off the MKS Controller.
3) Open the needle valve on the LPCI source at least four turns to increase the rate of air flow into the vacuum. Wait for ten minutes to let the turbomolecular pumps spin down.
4) Disconnect the glass inlet splitter from the source, and move it completely out of the way.
5) Disconnect the Teflon or polyethylene hoses from the inlet splitter.
6) Disconnect the thermocouple and power leads from the left end of the TAGA.
7) Disconnect the high voltage cable from the electrode.
8) Disconnect the pressure controller from the source. This will increase the rate air flows into the system.
9) Unhook the latch securing the source to the body of the TAGA. This will allow the source to separate slightly when the entire vacuum is gone. That separation is your indicator to proceed with the next step.
10) Once the source has partially separated from the TAGA body, release the cover over the multiplier control card on the right end of the TAGA, and release the end plate on the left end of the TAGA and pull out slightly. This will allow you to pull down the front cover of the TAGA.
11) Pull down the front cover of the TAGA, and let it down to its lowest position gently.
12) Remove the curtain gas tube from the back of the lower extension of the source by squeezing on the release tab and pulling free.
13) Remove the clamp connecting the vacuum hose to the bottom of the source, and place the clamp in a secure location.
14) Push the vacuum hose connector back slightly and let down to separate the connection. Carefully remove the o-ring and its internal metal support. Set the o-ring and metal support aside in a secure location.
15) Swing the source slightly away from the TAGA.
16) Support the bottom of the source with your left hand while you pull the hinge pin up and out of the hinge. Set the hinge pin in a secure location.

17) Carefully move the source away from the TAGA and place it in its secure storage location.

7.15.2 Installation of the APCI Source

1) Get the APCI source from its secure storage location.
2) Insert the hinge on the source into the hinge on the TAGA and insert the hinge pin (which was removed from the LPCI source and placed in a secure location).
3) As a precaution, use compressed nitrogen to blow through the orifice from the vacuum side of the source.
4) Swing the source against the TAGA and close the hasp on the front latch. This will hold the source in place.
5) Remove the inlet side of the source by unscrewing the knurled screw heads between the sections and pivoting the inlet side of the source up and off of its locator pin. Be very careful not to damage the needle projecting out of the right end of the inlet side of the source. This step is necessary to be able to close the plate at the end of the TAGA prior to completing installation.
6) Install the three color-coded high voltage leads into their color-coded holes in the lower portion of the APCI source.
7) Install the o-ring and its internal metal support, then the clamp joining the vacuum hose to the bottom of the source. Be very careful to make a good connection, making sure there are no small fibers on the seal.
8) Push the curtain gas supply tube onto the nipple at the back of the bottom of the source.
9) Double check to make sure the color-coded high voltage vacuum feed through connectors are correctly placed, and firmly installed.
10) Close the front cover of the TAGA.
11) Close and latch the cover over the multiplier supply board.
12) Close and secure the left end plate on the TAGA.
13) Reattach the inlet side of the source by carefully placing the hole in the top index tab over the pin in the top of the instrument side of the source, then swinging the inlet side down to contact with the seal. Be very careful of the needle during this process.
14) Screw in the knurled screw heads to secure the source parts together.
15) To get an acceptable seal, pull down on the left end of the source (not the glass tube!), and re-tighten the knurled screw heads.
16) Connect the high voltage lead from the extension on the back of the source to the hole in the left side plate on the TAGA. The longer connector goes into the hole in the source.
17) Attach the hose from the standard introduction splitter to the glass tube on the left end of the APCI.
18) Attach the hose to the SAF to the connector on the bottom of the APCI.
19) Turn on the two rough pumps under the TAGA, pausing about 15-seconds between turning on the first and turning on the second.
20) Wait five minutes!
21) Verify that the nitrogen supply is on.
22) Turn on the TAGA.

7.15.3 Removal of the APCI Source

1) Turn off the TAGA and both of the rough pumps
2) Turn off the MKS Controller.
3) Unhook the latch securing the source to the body of the TAGA. This will allow the source to separate slightly when the entire vacuum is gone. That separation is your indicator that you may disconnect the vacuum side of the source from the TAGA.
4) Unplug the high voltage cable from the left end panel of the TAGA.
5) Disconnect the hoses from the APCI, one from the glass tube on the left of the source, the other from the connector on the bottom of the source.
6) Loosen both knurled screw heads, one on the front of the source, the other on the back of the source. Since these nuts are normally very tight, it may be difficult to do this with your fingers. Each of the nuts is provided with a hole in its side through which the shaft of a 2.5 mm hex wrench can fit. It can be used as a handle to loosen the nut.
7) Rotate the left end of the inlet side of the source (do not use the glass tube as a handle!) Upward, then lift the unit off of the pin at the top of the vacuum side of the source. Set it aside in a secure location, being careful not to damage the needle.
8) Once the source has partially separated from the TAGA body due to loss of vacuum, release the cover over the multiplier control card on the right end of the TAGA, and release the end plate on the left end of the TAGA and pull out slightly.
9) Pull down the front cover of the TAGA.
10) Remove the curtain gas tube from the back of the lower extension of the source by squeezing on the release tab and pulling free.
11) Remove the clamp connecting the vacuum hose to the bottom of the source, and place the clamp in a secure location.
12) Push the vacuum hose connector back slightly and let down to separate the connection. Carefully remove the o-ring and its internal metal support. Set the o-ring and metal support aside in a secure location.
13) Unscrew the three color-coded high voltage vacuum feed-through connectors and replace them in the three holders on top of the turbomolecular pump controller under the left end of the TAGA vacuum housing.
14) Swing the source slightly away from the TAGA.
15) Support the bottom of the source with your left hand while pulling the hinge pin up and out of the hinge. Set the hinge pin in a secure location.
16) Carefully reconnect the two parts of the APCI source.
17) Carefully move the source away from the TAGA and place it in its secure storage location.

7.15.4 Installation of the LPCI Source

1) Get the LPCI source from its secure storage location.
2) Insert the hinge on the source into the hinge on the TAGA and insert the hinge pin (which was removed from the APCI source and placed in a secure location).
3) Swing the source against the TAGA and close the hasp on the front latch. This will hold the source in place.
4) Install the o-ring and its internal metal support, then the clamp joining the vacuum hose to the bottom of the source. Be very careful to make a good connection, making sure

there are no small fibers on the seal.

5) Push the curtain gas supply tube onto the nipple at the back of the bottom of the source.
6) Close the needle valve on the inlet nearly all the way.
7) Attach the pressure controller.
8) Turn on all the rough pumps. Be sure to include the rough pump for the pressure controller. Be sure to wait five minutes before turning on the TAGA.
9) Connect the inlet hose to the top of the inlet splitter, and the SAF hose to the bottom of the inlet splitter.
10) Attach the inlet splitter to the LPCI inlet.
11) Attach the power cord and the thermocouple connector from the LPCI to the end panel on the left side of the TAGA.
12) Connect the high voltage cable from the current source to the electrode.
13) Verify that the nitrogen supply is on.
14) Turn on the TAGA.

7.16 Cleaning the LPCI Source

The LPCI source is cleaned at the beginning of each field job, and should be done at least once each week of operation. Cleaning may be required much more frequently, depending on multiple factors. Brief exposure to certain substances can cause immediate contamination of the source, and that contamination can be so severe that immediate corrective action is necessary.

7.16.1 Known Contaminants Producing Immediate Degradation of LPCI Performance

A number of substances have been identified that have caused rapid degradation of LPCI performance, requiring physical cleaning of the source to allow continued operations. Some of these contaminants include:

- Un-baked Tedlar bags
- Strong paint fumes (performing indoor monitoring in the presence of open paint cans and during painting operations)
- Monitoring in smoke plumes
- Use of strong hand lotions (Keri Lotion)

7.16.2 Symptoms Indicating Need for Cleaning the LPCI Source

There are a number of indications that the LPCI source needs cleaning, and the nature of these indications provides clues as to what portion of the source has been most contaminated and therefore needs special attention:

- Sudden, complete or nearly complete loss of ions
- Decreasing ion intensity with time after the start of a run when providing a constant concentration of a target substance
- Loss of linearity during calibrations, particularly for the heavier compounds
- Gradual loss of response factor during the day

7.16.3 LPCI Source Cleaning Procedure

1) Shut down the TAGA as detailed in 7.2, except delete step 11. Leave the needle valve open enough to maintain a pressure of at least 2 Torr inside the source.
2) Turn off power to the TAGA. Wait five minutes, then turn off power to both rough pumps.
3) Wait five more minutes for the turbomolecular pumps to spin down, then open the needle valve enough to register at least 5 Torr.
4) Disconnect the high voltage cable from the LPCI electrode.
5) Disconnect the heater and thermocouple plugs from the end of the TAGA.
6) Disconnect the glass splitter from the source inlet, and swing the glass away from the source.
7) Disconnect the pressure controller from the source, then close the needle valve on the source.
8) Open the cover over the electron multiplier.
9) Open the cover under the LPCI source.
10) Open the front cover of the TAGA, being careful to let it down gently to avoid breaking the hinges.
11) Disconnect the quick connect on the nitrogen supply line where it attaches to the bottom of the LPCI source.
12) Unscrew the clamp that attaches the vacuum hose to the bottom of the LPCI source, and carefully disconnect the hose, being sure to recover the o-ring seal.
13) Open the clamp that holds the LPCI source to the TAGA.
14) Once the TAGA is at atmospheric pressure, swing the source open, hold the source firmly in one hand and pull out the hinge pin, releasing the LPCI source from the instrument.
15) Place the LPCI source, with the electrode up, on a flat, clean area.
16) Remove the electrode, and clean the oxidized metal from the tip and side of tip using abrasive, and then set aside.
17) Use cotton swabs slightly moistened with methanol to clean possible deposits off of the Q0 rods, making sure to include all of the surfaces around the outside of each rod.
18) Use cotton swabs slightly moistened with iso-octane (2,2,4-trimethylpentane) to clean possible deposits off of the Q0 rods, making sure to include all of the surfaces around the outside of each rod.
19) Cut a ¼-inch wide strip of one of the finer abrasives on acetate backing (either light tan or green) and hold the strip at each end with a hemostat. Use the abrasive strip to 'shoe polish' the Q0 rod surfaces that face the interior of the ion path.
20) Repeat steps 17 and 18, using as many swabs as needed until the swabs are visibly clean after use.
21) Turn the LPCI source over, with the high vacuum side up.
22) Clean the vacuum side of the well around the orifice with cotton swabs lightly moistened with methanol, scrubbing strongly.
23) Clean the vacuum side of the well around the orifice with cotton swabs lightly moistened with iso-octane, scrubbing strongly.
24) Turn the LPCI source over, with the high vacuum side down.
25) If the symptom indicating the necessity of cleaning included the sharp reduction or lack of ion production, lightly moisten a cotton swab with methanol, and very lightly dust the cotton with finely powdered alumina abrasive. Clean the inside of the 'well' with the

abrasive-dusted cotton swab.

26) Use cotton swabs slightly moistened with methanol to clean possible deposits from the inside of the 'well'.
27) Use cotton swabs slightly moistened with iso-octane (2,2,4-trimethylpentane) to clean possible deposits from the inside of the 'well'.
28) Reassemble the LPCI source. Replace the LPCI source onto the TAGA, reversing the procedure used for removing the source.
29) Turn on the first rough pump, wait 30-seconds.
30) Turn on the second rough pump, wait five minutes.
31) Verify that the nitrogen supply is on.
32) Turn on power to the TAGA, and check to be sure the green light on the end is blinking.
33) Turn on the computer.
34) Load Tune.
35) In about half an hour, the instrument will be ready to resume work.

7.17 Cleaning the APCI Source

The APCI source is cleaned at the beginning of each field job, and should be done at least once each week of operation. Cleaning may be required much more frequently, depending on multiple factors. The APCI orifice is only 0.1 mm in diameter, and plugs quite easily. Brief exposure to certain substances can cause immediate contamination of the source, and that contamination can be so severe that immediate corrective action is necessary.

7.17.1 Known Contaminants Causing Immediate Degradation of the APCI Performance

A number of substances have been identified that have caused rapid degradation of APCI performance, some of which require physical cleaning of the source to allow continued operations. Some of these contaminants include:

- Ammonia and related substances, such as glass cleaners
- Alcohols and alcohol-containing substances, such as glass cleaners and stick deodorants

7.17.2 Symptoms Indicating Need for Cleaning the APCI Source

There are a number of indications that the APCI source needs cleaning, and the nature of these indications provides clues as to what portion of the source has been most contaminated and therefore needs special attention:

- Sudden, complete or nearly complete loss of ions. This usually indicates that the orifice has become plugged or nearly plugged.
- Decreasing ion intensity with time after the start of a run when providing a constant concentration of a target substance
- Momentary or periodic reduction in background signal
- Gradual loss of response factor during the day

7.17.3 APCI Source Cleaning Procedure

In many cases, all that is needed is to unplug the orifice. This is done by blowing

nitrogen backward through the orifice after removing the source from the body of the TAGA. However, at least once each week during heavy use, it is advisable to do a relatively complete cleaning as detailed below.

1) Shut down the computer.
2) Turn off power to the TAGA. Wait five minutes, then turn off power to both rough pumps.
3) Disconnect the APCI high voltage cable.
4) Open the cover over the electron multiplier.
5) Open the cover under the APCI source.
6) Open the front cover of the TAGA, being careful to let it down gently to avoid breaking the hinges.
7) Unscrew the two knurled nuts that hold the atmospheric pressure section of the APCI source to the vacuum interface and separate the sections, setting the atmospheric pressure section aside, making sure to protect the needle.
8) While air is bleeding into the system, (a process that can take over 30-minutes) detach the curtain gas supply by disconnecting the quick connect from the side, then unscrew the three electrical feed-through from the bottom of the source.
9) Open the latch on the side of the source, and wait for sufficient air to bleed into the system to release the source.
10) Clean the Q0 rods following the procedure provided from the instructions for cleaning the LPCI source, steps 17 through 20.
11) Clean the high pressure side of the face of the source with slightly dampened wipes, alternating between the two solvents.
12) Turn the source over to expose the high vacuum side.
13) Carefully remove the four cap screws holding in the skimmer cone.
14) Carefully use the blade of a jeweler's screwdriver inside one of the screw holes to loosen the cone.
15) If possible, lift out the cone, otherwise, turn the source over and gently tap the source down on a clean surface. The cone should fall out.
16) Use a fine abrasive to clean the outer portion of the skimmer cone near the tip – it may be very dirty. Also, gently clean the tip of the cone. Inspect the tip of the cone with a ten-power magnifier to be sure it is clean and even.
17) Clean the inside of the skimmer cone with dampened cotton swabs, using the same process as used on the Q0 rods.
18) <u>Very</u> gently use the tip of a slightly moistened cotton swab to clean the inside edge of the ring (just above the orifice), and the orifice itself. The center portion of the orifice is very thin, and easily damaged. Use both solvents as before.
19) Use a wet swab to place a small drop of iso-octane on the orifice, and then quickly blow it down through the orifice with compressed nitrogen.
20) Reassemble the vacuum interface, and then put it back on the TAGA.
21) Reconnect the curtain gas supply and the wires, making sure the three wires are each attached correctly in accordance with the color coded fittings.
22) Place a septum over the orifice, and start the rough pumps while holding the septum in place long enough for the vacuum to hold it in place.
23) Wait five minutes.
24) Verify that the nitrogen supply is on, and then turn on the TAGA.
25) Start the computer.

26) Load TUNE, and make sure the APCI ACTIVE REST state is selected (this will assure that curtain gas continues once the READY status is achieved. Note that the septum will likely blow off once the TAGA is started.
27) Click on the Instrument Status, and select [OPTIONS], [DETAILED STATUS].
28) While the TAGA is pumping down, remove, inspect and clean the gold needle, then replace the needle.
29) Reattach the atmospheric pressure portion of the source by hooking the top over the pin on top of the vacuum interface and screwing in the knurled screws. Be sure to tighten by pulling down firmly on the end of the source while tightening the screws.
30) Re-adjust the position of the needle.
31) Finish reassembling the inlet hoses, and re-start the SAF.

8.0 CALCULATIONS

All calculations, including calibration curves, response factors, intercepts, detection limits, and average concentrations over specified time intervals are performed by the software and are presented in Appendix B. The target compound calculation is presented in Table 3, Appendix B. All target compound concentrations are reported to two significant figures.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

The following quality assurance/quality control (QA/QC) protocols apply to this procedure. The QA/QC requirements in this section may be waived by the Work Assignment Manager (WAM) or their designee depending on the data quality objectives of the project. All waivers must be documented in field logbooks or on a Work Assignment field Change Form.

9.1 MS/MS Mass Calibration

At the beginning of each day, prior to any monitoring event, a standard(s) mixture is introduced by a calibrated MFC into the SAF. The tuning parameters for the first quadrupole atomic mass units (amu) and the third quadrupole amu are optimized for sensitivity and mass assignment. The peak widths are limited between 0.55 amu and 0.85 amu. The mass assignments are set to the correct values within 0.15 amu.

9.2 Standard Calibration

A beginning of day (BOD) and end of day (EOD) calibration must be performed using a zero point and a minimum of five standard concentrations before and after the monitoring period. The calibration is acceptable if the correlation coefficient of each ion pair is greater than or equal to 0.90. Depending on environmental and instrumentation factors, calibrations may be repeated prior to any monitoring survey.

9.3 Response Factor/Intermediate Response Factor

Target compound concentrations are quantitated using the compound's response factor (RF) generated during calibration. An intermediate response factor (IRF) is calculated between a pair of calibrations, such as BOD and EOD calibrations. A percent difference (%D) of the

compound's RF is calculated between pairs of calibrations. If %D is greater than 25%, the IRF must be used to quantify the target compound.

9.4 Detection and Quantitation Limits

The initial ambient air data segment collected at the beginning of each monitoring period and the RF or IRF are used in calculating detection and quantitation limits. The detection limit concentration is defined as three times the standard deviation of the concentration at a compound's ion pair's zero point on the calibration curve. The quantitation limit concentration is defined as ten times the standard deviation of the concentration at the same point.

9.5 Target Compound Evaluation

Review all ion chromatograms for each target compound for coincidence of concentrations. Note all incidents of disagreement among concentrations provided by ion pairs for each target compound.

If one or more ion pairs for the same target compound show signs of interference, delete those ion pairs from data processing, and re-process the run. Be sure to note the elimination of the ion pairs in the report dialog. If one ion pair for a target substance is significantly lower than the other associated ion pairs, and if the 30 mL spike of the target substance has all of the associated ion pairs at the same level as each other, report the concentration indicated by the lowest ion pair during the monitoring run.

Note other interferences and data issues that may have been included in the operator's notes on the TAGA flag table sheets. In some cases, this may include the presence of items that may have caused elevated levels at a monitoring location, or the presence of negative interferences.

9.6 Tedlar Bag Replicate Analysis

One sample replicate should be analyzed after every ten samples. The sample should be randomly chosen and re-analyzed. Calculate the relative percent difference (RPD) for any concentration detected. The RPD is given as the absolute difference between the replicate values divided by their mean, expressed as a percentage. The acceptance criteria for RPD is $^{\pm}$35%.

9.7 Tedlar Bag Blanks

The blanks should not contain any target compound at concentrations above the limit of quantitation (lowest standard in the initial calibration). If contamination is a problem, the source of the contamination must be investigated. Appropriate corrective actions should be taken and documented.

If any compound detected in the blank is also detected in the associated samples, those sample results are to be flagged as possibly contaminated.

10.0 DATA VALIDATION

The data is reviewed using the QA/QC considerations listed in Section 9.0 by the analyst prior to submittal to the client to ensure that the instrument has been operated in accordance with this SOP and manufacturer's recommendations and that all QA/QC checks have been performed. The Screening data objective requires that the calibration and detection limits be evaluated. All the field analytical reports must be reviewed in accordance with Administrative Procedure (AP) #22, *Peer Review of SERAS Deliverables.*

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow Environmental Protection Agency (EPA), Occupational Safety and Health Administration (OSHA), and corporate health and safety practices.

12.0 REFERENCES

1. *Love Canal Full-Scale Air Sampling Study Quality Assurance Project Plan*, Response Engineering and Analytical Contract (REAC), July 1987.

2. *API Series Operator's Manual*, Perkin-Elmer Sciex Instruments, Foster City, CA, February 1997.

3. *MKS Type 146C Cluster Gauge Vacuum Gauge Measurement and Control System, Instruction Manual, Revision B*, MKS Instruments, Wilmington, MA, March 1999.

4. *PHD 22/2200 Syringe Pump Series User's Manual*, Harvard Apparatus, Inc., Publication 5400-008-REV-E, Holliston, MA.

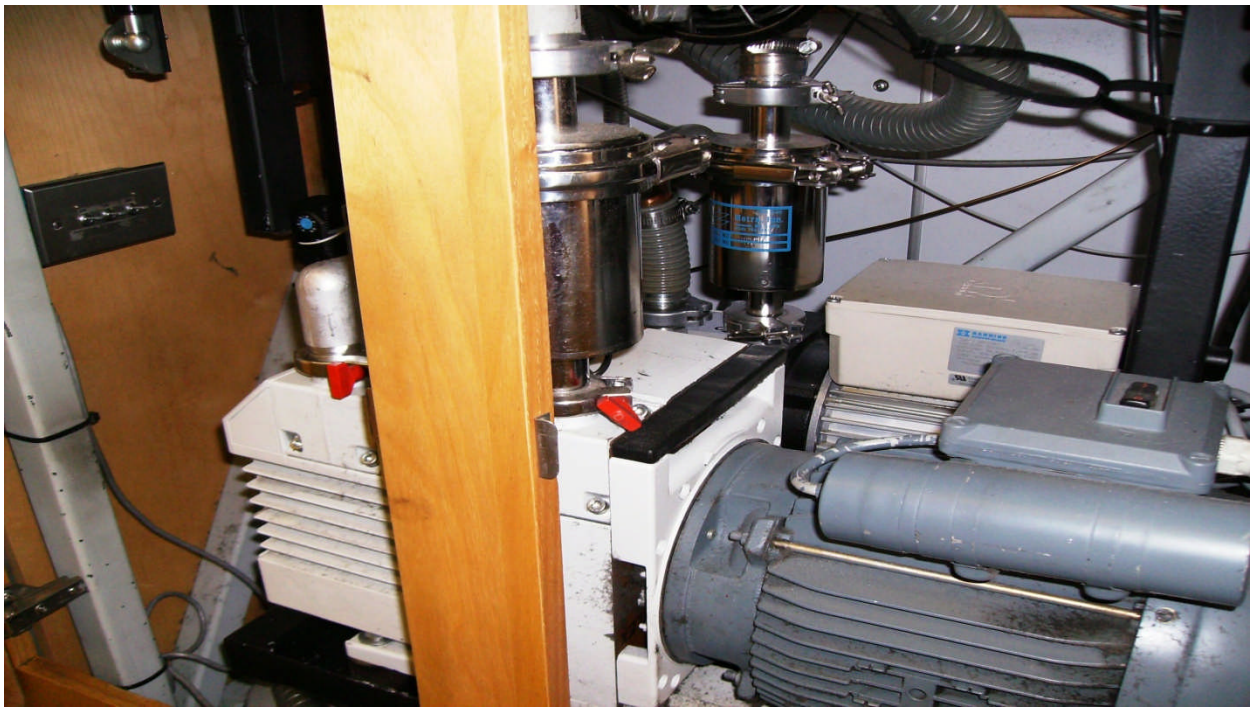
13.0 APPENDICES

A Pictures
B Tables
C Advanced Tuning Notes
D MKS 146C Cluster Gauge Controller Operation
E Harvard Syringe Pump Operation
F System File Management
G Screen Capture
H Chlorine and Chlorine Dioxide

APPENDIX A
Pictures
SOP #1711
Date February 2011

Picture 1 Location of the TAGA IIe in the mobile laboratory (Bus 1553). The gas cylinders are on the right, and the TAGA IIe is in the center of the picture.

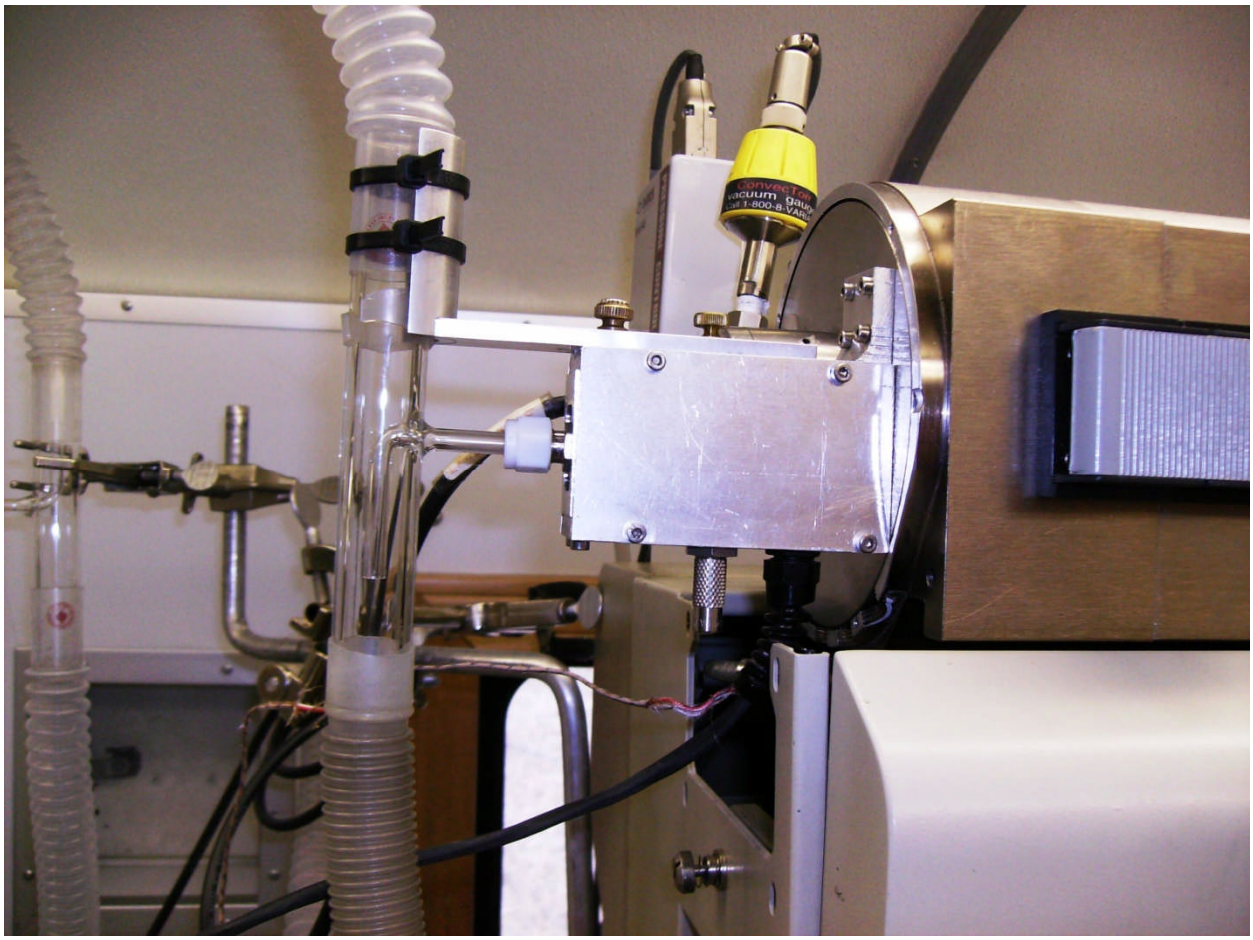
Picture 2 Pictured is the forward end of the instrument, with the red power rocker-switch, and the two indicator lights. The upper, green light is on, indicating that the instrument is in a normal operating condition.



Picture 3 Located in the cabinet under the TAGA IIe are two rough pumps, one which is attached to the two turbomolecular pumps in the TAGA IIe, and the other which provides vacuum for the source vacuum interface. To the left in the picture are three switches, these provide power to the two rough pumps and the TAGA IIe instrument.

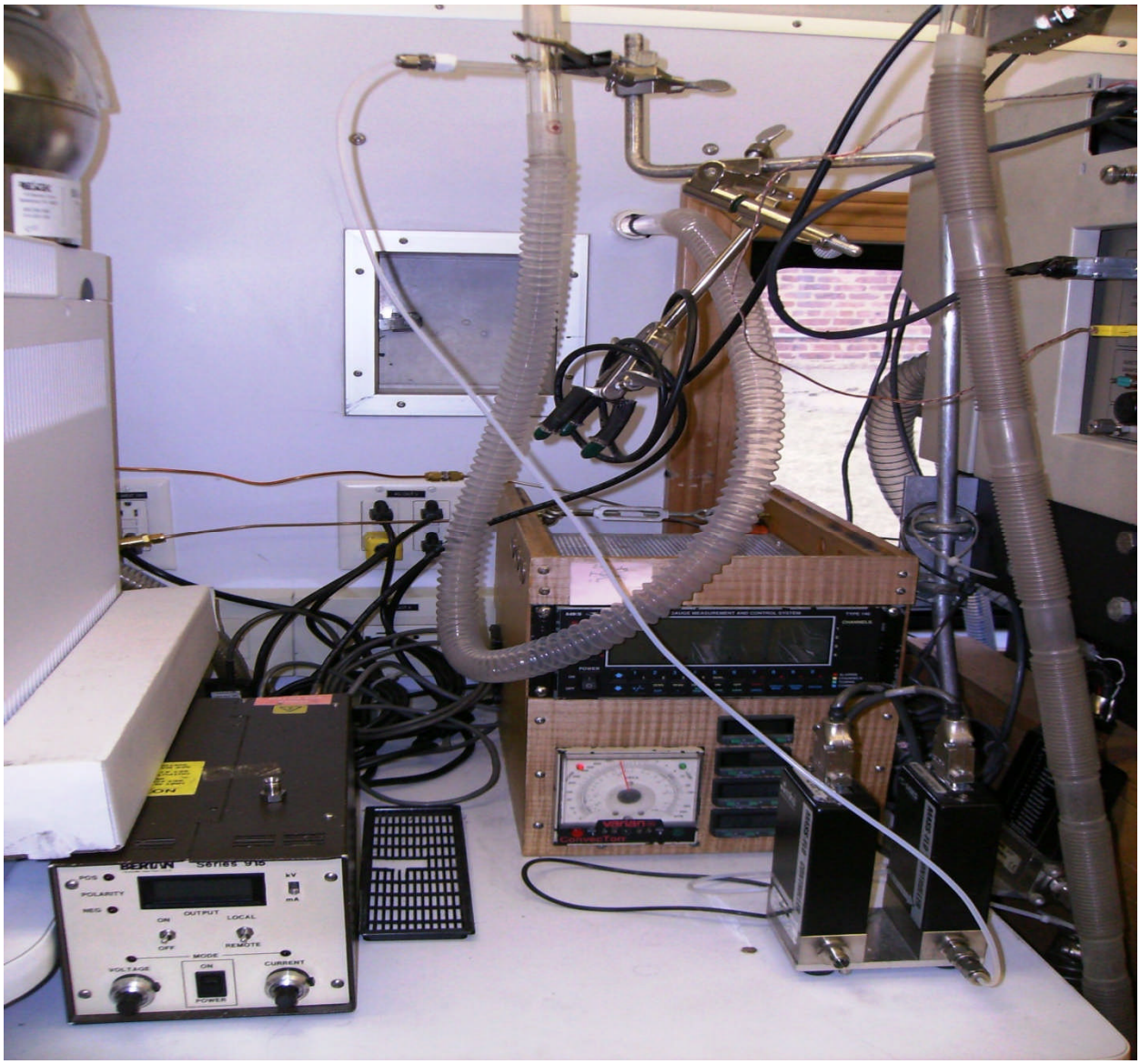
Picture 4 Close-up of the switch box with the three power switches.

Picture 5 Depicted is the configuration of an installed LPCI source on the TAGA IIe. Starting from the left of the picture is the source pressure controller. The Swagelok fittings and Teflon tubing to its left are going to a rough pump located in cabinet below the GC/MS unit. To the right of the controller is the analog pressure sensor (yellow device). To the far right is the glass splitter attached to the LPCI inlet with a Teflon nut. The Teflon tubing attached at the top of the glass splitter provides sample air flow (SAF) from the outside of the laboratory. The tubing below the glass splitter goes to a blower and mass flow controller through a particulate filter. The blower exhausts outside through the floor of the laboratory.

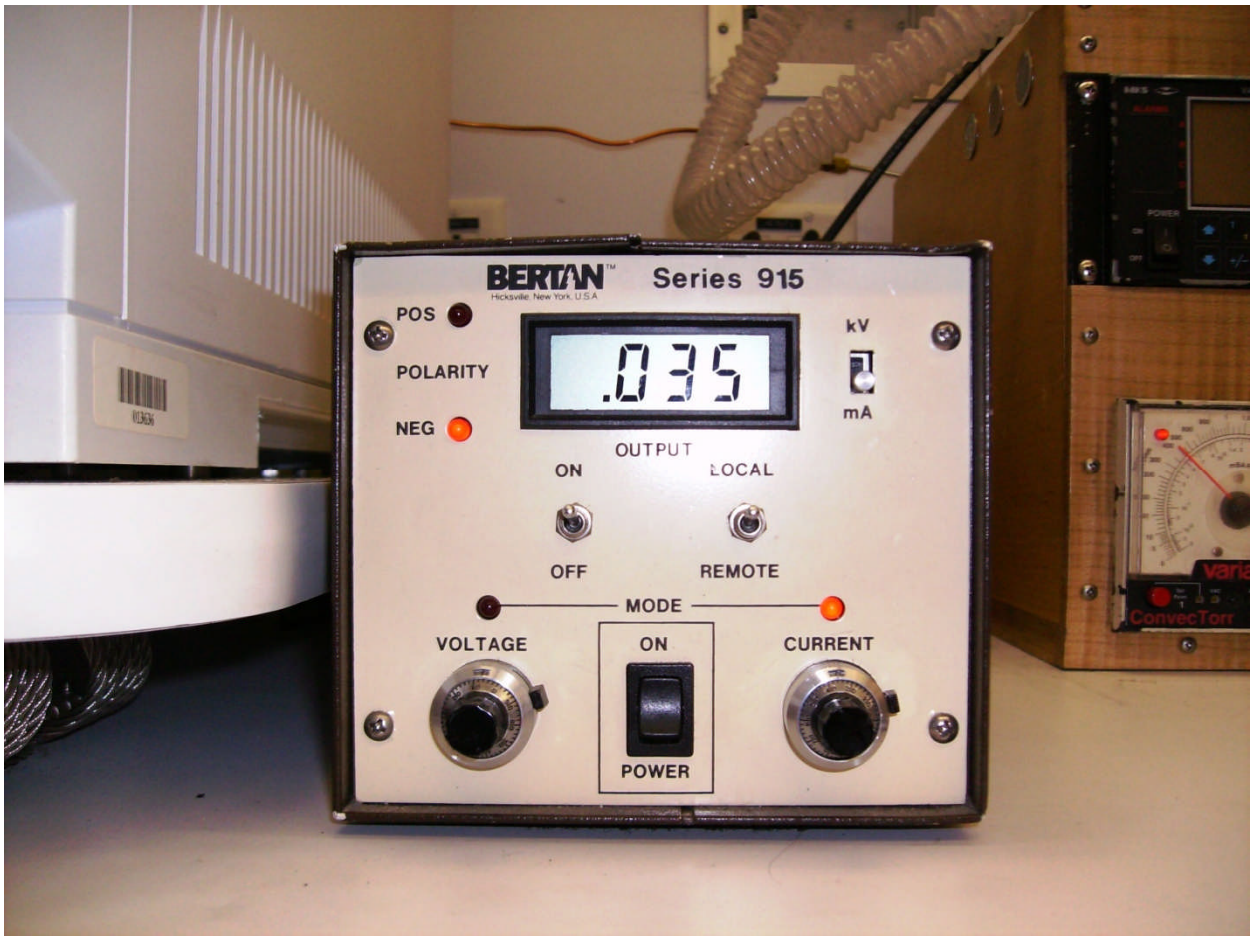


Picture 6 Side view of the LPCI source with glass splitter attached. At bottom of the LPCI inlet can be seen the handle of a needle valve. This is used to adjust the flow of air into the source.

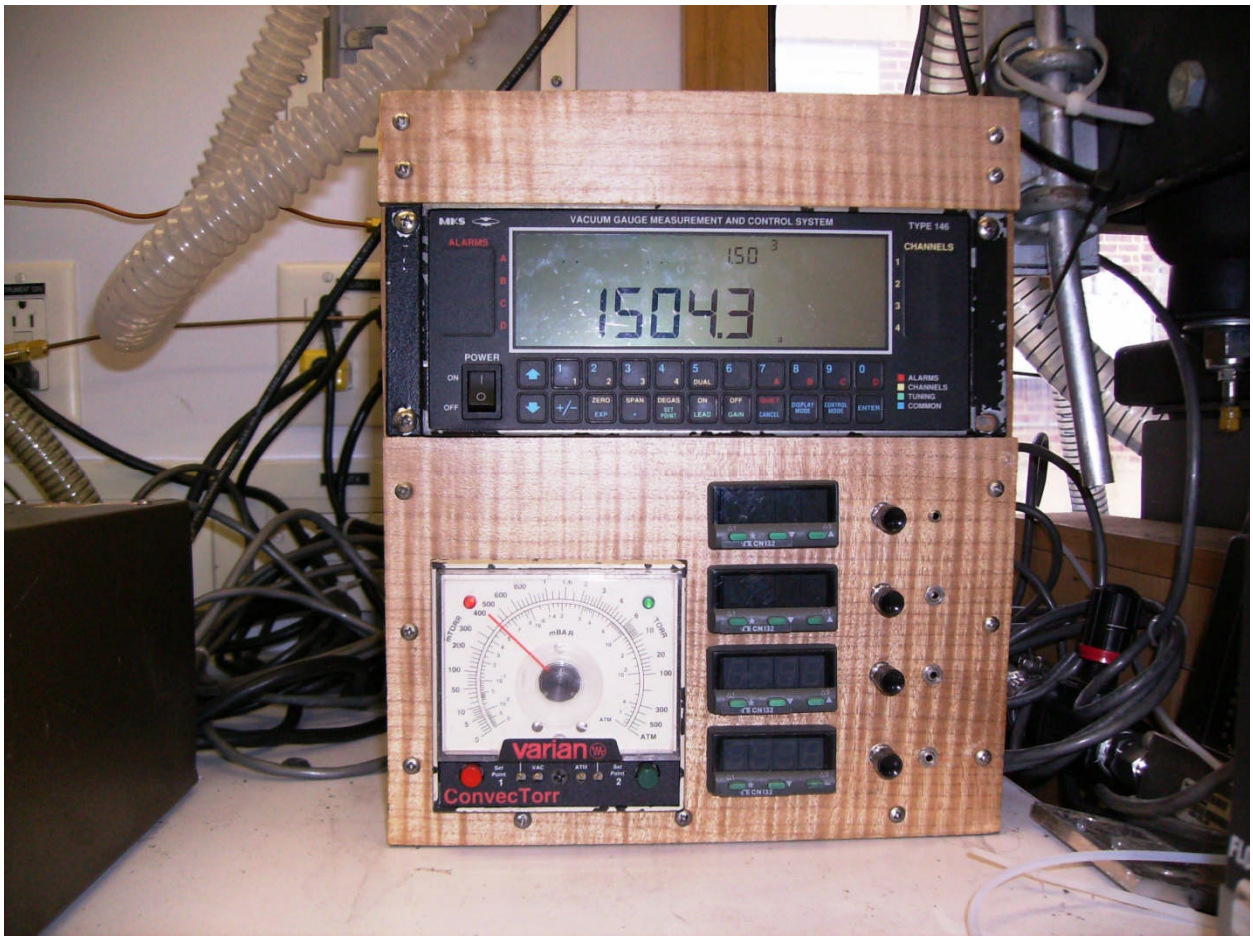
Picture 7 Depicted are contents of cabinet below the GC/MS unit. To the right are two rough pumps, one is used by the pressure controller and the other by the GC/MS. Seen on the left is the GC/MS uninterruptable power supply (UPS). Located in this cabinet is the second blower for the SAF.



Picture 8 Depicted is the arrangement of the auxiliary equipments between the TAGA IIe and the GC/MS unit. At the front left is the power supply for the LPCI electrode. At the front right are two mass flow controllers (MFCs) used to control the flow of standard into the upstream flow of the glass splitter. A 1/8-inch Teflon line leads from one of the MFCs to the glass splitter. At the top of this standard introduction glass splitter is Teflon tubing (not shown). The other end of the Teflon tubing is attached to the top of the glass splitter attached to the LPCI source (not shown. Behind the MFCs is a box containing a MKS 146c Gauge Controller, an analog pressure gauge, and a set of four auxiliary temperature controllers.



Picture 9. Close up of the Bertan Series 915 power supply. This is used to provide a constant current to the electrode of the LPCI source.



Picture 10. Close up of the box containing the MKS 146c controller, the Varian ConvecTorr analog pressure gauge, and four temperature controllers. The analog pressure gauge provides readings from the analog pressure sensor located between the pressure controller and the LPCI source.

Picture 11. Close up of the MKS 146c Controller

Picture 12. Close up of three MKS MFCs. The two on the right are used to control the flow of standard gases and the one behind and to the left is used to control the flow of air going through the SAF blower.

APPENDIX B
Tables
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TABLE 1. MRM Table

Compound	Display	Q1 Mass	Q3 Mass
1,1,1-TRICHLOROETHANE	1,1,1-TCA 97/61	97	61
1,1,1-TRICHLOROETHANE	1,1,1-TCA 99/61	99	61
1,1,1-TRICHLOROETHANE	1,1,1-TCA 99/63	99	63
DICHLOROETHENE	DCE 96/61	96	61
DICHLOROETHENE	DCE 98/61	98	61
DICHLOROETHENE	DCE 98/63	98	63
BENZENE	BENZENE 78/39	78	39
BENZENE	BENZENE 78/52	78	52
CHLORINE	CHLORINE 70/35	70	35
CHLORINE	CHLORINE 72/37	72	37
CHLORINE	CHLORINE 72/35	72	35
CHLORINE	CHLORINE 74/37	74	37
CHLORINE DIOXIDE	ClO2 67/67	67	67
CHLORINE DIOXIDE	ClO2 67/51	67	51
CHLORINE DIOXIDE	ClO2 69/69	69	69
CHLORINE DIOXIDE	ClO2 69/53	69	53
CHLOROBENZENE	CLBNZ 112/51	112	51
CHLOROBENZENE	CLBNZ 112/77	112	77
CHLOROBENZENE	CLBNZ 114/77	114	77
FREON 22	F-22 85/50	85	50
FREON 22	F-22 87/50	87	50
FREON 22	F-22 85/51	85	51
FREON 22	F-22 87/51	87	51
FREON 22	F-22 85/66	85	66
MTBE	MTBE 89/41	89	41
MTBE	MTBE 89/39	89	39
MTBE	MTBE 73/43	73	43
PINENE	PINENE 107/105	107	105
TETRACHLOROETHENE	PCE 164/94	164	94
TETRACHLOROETHENE	PCE 164/129	164	129
TETRACHLOROETHENE	PCE 166/129	166	129
TETRACHLOROETHENE	PCE 166/131	166	131
TRICHLOROETHENE	TCE 130/60	130	60
TRICHLOROETHENE	TCE 130/95	130	95
TRICHLOROETHENE	TCE 132/95	132	95
TRICHLOROETHENE	TCE 132/97	132	97

TABLE 1. (cont) MRM Table

Compound	Display	Q1 Mass	Q3 Mass
TOLUENE	TOLUENE 92/91	92	91
TOLUENE	TOLUENE 92/65	92	65
TOLUENE	TOLUENE 92/77	92	77
TOLUENE	TOLUENE 92/39	92	39
TOLUENE	TOLUENE 92/51	92	51
VINYL CHLORIDE	VC 62/27	62	27
VINYL CHLORIDE	VC 64/27	64	27
XYLENE	XYLENE 106/51	106	51
XYLENE	XYLENE 106/65	106	65
XYLENE	XYLENE 106/91	106	91
METHYLENE CHLORIDE	MeCl2 83/48	83	48
METHYLENE CHLORIDE	MeCl2 85/48	85	48
METHYLENE CHLORIDE	MeCl2 85/50	85	50
METHYLENE CHLORIDE	MECL 83/47	83	47
METHYLENE CHLORIDE	MECL 85/47	85	47
METHYLENE CHLORIDE	MECL 85/49	85	49
CHLOROFORM	CHCL3 83/47	83	47
CHLOROFORM	CHCL3 85/47	85	47
CHLOROFORM	CHCL3 85/49	85	49
1,1,2,2-TETRACHLOROETHANE	1122TECA 83/47	83	47
1,1,2,2-TETRACHLOROETHANE	1122TECA 85/47	85	47
1,1,2,2-TETRACHLOROETHANE	1122TECA 130/95	130	95
1,1,2,2-TETRACHLOROETHANE	1122TECA 132/97	132	97
METHYL MERCAPTAN	MESH	48	33
METHYL MERCAPTAN	MESH	50	15
METHYL MERCAPTAN	MESH	50	35
2-CHLORO-6-FLUOROPHENOL	CLFPH	146	63
2-CHLORO-6-FLUOROPHENOL	CLFPH	146	82
2-CHLORO-6-FLUOROPHENOL	CLFPH	146	98
2-CHLORO-6-FLUOROPHENOL	CLFPH	148	63
2-CHLORO-6-FLUOROPHENOL	CLFPH	148	82
2-CHLORO-6-FLUOROPHENOL	CLFPH	148	100
1,3-BUTADIENE	13BDE 54/39	54	39
1,3-BUTADIENE	13BDE 54/54	54	54
1,2-DICHLOROETHANE	12DA 62/27	62	27
1,2-DICHLOROETHANE	12DA 64/27	64	27
1,2-DICHLOROETHANE	12DA 99/63	99	63
1,2-DICHLOROETHANE	12DA 101/65	101	65

TABLE 1. (cont) MRM Table

Compound	Display	Q1 Mass	Q3 Mass
1,2-DICHLOROPROPANE	12DCPA 62/27	62	27
1,2-DICHLOROPROPANE	12DCPA 76/39	76	39
1,2-DICHLOROPROPANE	12DCPA 76/41	76	41
1,2-DICHLOROPROPANE	12DCPA 113/41	113	41
1,2-DICHLOROPROPANE	12DCPA 113/49	113	49
1,2-DICHLOROPROPANE	12DCPA 113/77	113	77
1,3-DICHLOROPROPENE	13DCPE 110/75	110	75
1,3-DICHLOROPROPENE	13DCPE 112/75	112	75
CARBON TETRACHLORIDE	CCL4 117/82	117	82
CARBON TETRACHLORIDE	CCL4 119/84	119	84
CARBON TETRACHLORIDE	CCL4 121/84	121	84
1,2-DIBROMOETHANE	EDB 188/109	188	109
1,2-DIBROMOETHANE	EDB 190/109	190	109

TABLE 2. Linear Regression Calibration Equations

A calibration curve of at least five concentrations must be constructed for each target compound. A straight line equation in the form of y = (m) (x) + b is fit to the standards raw data.

$$y = mx + b$$

where:
- y = Instrument response in ion counts per second (ICPS)
- m = Slope of the line in ICPS/ part per billion by volume (ppbv)
- x = Concentration of the calibration standard in ppbv
- b = y-intercept in ICPS.

The (x), or the unknown concentration of a compound, is determined by rearranging the straight line equation as shown below. Non-linear data is indicative of the detector response limitations and/or the interferences.

$$x = \frac{y - b}{m}$$

where:
- x = target compound's concentration in part per billion by volume (ppbv).
- y = target compound's response in ion counts per second (ICPS).
- b = target compound's y-intercept in ICPS.
- m = target compound's response factor in ICPS/ppbv.

The mathematical equivalent of the Method of Standard Addition is used during calibration procedures of the TAGA MS/MS. The linear least square fit is calculated, providing both slope and intercept. During subsequent calculations, the calculated slope is used, and the intercept is assumed at zero, converting the background level to an assumed zero. The concentrations calculated are the amounts in excess of the background level.

TABLE 3. Concentration Calculation

Concentration for each ion pair utilized during monitoring of a target compound is calculated as follows:

$$C_s = \frac{Target\ compound's\ response\ in\ ICPS}{Target\ compound's\ response\ \ factor\ in\ ICPS/ppbv}$$

where:
C_s = Compound ion pair concentration in part per billion by volume (ppbv)
$ICPS$ = Ion counts per second

The compound concentration is then generated by averaging the concentration of the compound's ion pairs as follows:

$$C_x = \frac{C_{s1} + C_{s2} + \ldots.. + C_n}{n}$$

where:
C_x = Compound concentration (ppbv)
C_{s1} = Compound concentration of first ion pair (ppbv)
C_{s2} = Compound concentration of second ion pair (ppbv)
C_n = Compound concentration of nth ion pair (ppbv)
N = Number of ion pairs to be averaged

The result concentration reported during surveys is generated by averaging all the compound's concentration (C_x) detected two flag intervals.

TABLE 4. Calculating Intermediate Response Factors

Intermediate response factors (IRFs) are used when initial and final response factors used in a data set differ by more than 25 percent. The following equation is used to calculate intermediate response factors:

$$IRF = \frac{2(RF_1 \times RF_2)}{(RF_1 + RF_2)}$$

where:

IRF	=	Intermediate response factor (icps/ppbv)
RF_1	=	The RF for an ion pair measured during the initial calibration event (icps/ppbv)
RF_2	=	The RF for the same ion pair measured during the final calibration event (icps/ppbv)

TABLE 5. Detection Limit Calculations

The detection limit (DL) concentration is defined as three times the standard deviation at a compound's ion pair zero point on the calibration curve. The initial ambient air collected at the beginning of each sampling period and the intermediate response factors for the sampling period are used to calculate the detection limits. The equation is as follows:

$$DL = \frac{3 \times SD}{RF \text{ or } IRF}$$

where:
- DL = Detection limit for an ion pair in part per billion by volume (ppbv)
- SD = Standard deviation of the ion intensity measured in an ambient air sample in ion counts per seconds (icps)
- RF = Response factor for an ion pair (icps/ppbv)
- IRF = Intermediate response factor for an ion pair (icps/ppbv)

The compound's DL is generated by averaging all the DLs of the compounds' ion pairs. The following equation is used to calculate the compound's detection limit:

$$DL_c = \frac{DL_1 + DL_2 + \ldots + DL_n}{n}$$

where:
- DL_c = Detection limit for a compound (ppbv)
- DL_1 = Detection limit for the first ion pair (ppbv)
- DL_2 = Detection limit for the second ion pair (ppbv)
- DL_n = Detection limit for the nth ion pair (ppbv)
- n = Number of ion pairs to be averaged

TABLE 6. Quantitation Limit Calculations

The quantitation limit (DL) concentration is defined as ten times the standard deviation at a compound's ion pair zero point on the calibration curve. The initial ambient air collected at the beginning of each sampling period and the intermediate response factors for the sampling period are used to calculate the detection limits. The equation is as follows:

$$QL = \frac{10 \times SD}{RF \text{ or } IRF}$$

where:
- QL = Quantitation limit for an ion pair in part per billion by volume (ppbv)
- SD = Standard deviation of the ion intensity measured in an ambient air sample in ion counts per seconds (icps)
- RF = Response factor for an ion pair (icps/ppbv)
- IRF = Intermediate response factor for an ion pair (icps/ppbv)

The compound's QL is generated by averaging all the QLs of the compounds' ion pairs. The following equation is used to calculate the compound's detection limit:

$$QL_c = \frac{QL_1 + QL_2 + \ldots + QL_n}{n}$$

where:
- QL_c = Quantitation limit for a compound (ppbv)
- QL_1 = Quantitation limit for the first ion pair (ppbv)
- QL_2 = Quantitation limit for the second ion pair (ppbv)
- QL_n = Quantitation limit for the nth ion pair (ppbv)
- n = Number of ion pairs to be averaged

TABLE 7. Error Bar Calculation

The potential maximum concentration percent deviations are symmetrical measurements of the concentration variance resulting from response factor variability. They represent the potential bias in the concentration due to changes in instrument sensitivity. "Error bars" are calculated using the following equation:

$$error\ bar = \frac{|RF_1 - RF_2|}{(RF_1 + RF_2)} \times 100$$

where: error bars = Maximum concentration percent deviation (unit less)
RF_1 = The RF for an ion pair measured during the initial calibration event (icps/ppbv)
RF_2 = The RF for the same ion pair measured during the final calibration event (icps/ppbv)

TABLE 8. Transport Efficiency Calculation

The following equation is used to calculate the transport efficiency:

$$\%\ Transport\ Efficiency = \frac{Signal\ intensity\ at\ the\ distal\ end\ of\ the\ hose}{Signal\ intensity\ at\ the\ proximal\ end\ of\ the\ hose} \times 100$$

The transport efficiency acquisition also provides the residence time, the time required for a sample to be transported through the Teflon hose. The residence time is obtained by observing the time required for the signal to reappear after the three-way valve is switched from introducing the target compound at a location adjacent to the heated transfer line to a location near the Teflon hose inlet.

APPENDIX C
Advanced Tuning Notes
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February 2011

ADVANCED TUNING NOTES

Optimizing Inlet Conditions and Lens Voltages

Most of the lens voltage adjustments are similar for both the APCI and LPCI modes, but there are a few distinct differences. The LPCI has a reduced pressure ionization chamber and the pressure is adjusted with a needle valve between the ranges of 1.0 to 3.0 Torr. The absolute and relative response factors of various substances are quite variable within this range. A pressure difference of 0.1 Torr can make a 20% difference in the response factor for some aromatics. Additionally, the source current for the LPCI is externally controlled and has a very significant effect on the relative response factors. The APCI has an orifice plate and a focusing ring (not present on the LPCI), both of which have very significant effects on the analytes.

LPCI inlet produces ionization by creating a glow discharge within a cell at pressures of 2.5 to 4.5 Torr, and requires less than 10 mL/min of air flow into the instrument. The APCI produces ionization with a high voltage discharge from a needle at atmospheric pressure. The air flow into the reaction chamber of the APCI head is 1500 mL/sec (90,000 mL/min). The LPCI reacts to changes in the concentration of target substances at the instrument inlet in 5 to 10 seconds (due to the transit time from the manifold to the electrode) while the APCI responds in a fraction of a second.

This section discusses the elements unique to the LPCI, the APCI, and those shared by both modes of operation. In general, the ranges and settings mentioned in this section are recommendations, not requirements. The operator must consider the set of target compounds and work out the best compromise for the analysis on a case by case basis.

LPCI Tuning

1) The LPCI source does not have an orifice plate or focusing ring, so the orifice plate (OR) and focusing ring (RNG) values in the State File will be zero.
2) The source pressure, which is controlled by the needle valve at the LPCI inlet, is set in the range of 1.0 to 3.0 Torr. There is a strong relationship between source pressure and signal strength for most aromatic compounds, with higher pressures producing much higher count rates. However, chlorinated ethenes are less sensitive to pressure changes and vinyl chloride tends to maximize at lower pressures.
3) The curtain gas setting is usually four and collision gas set at 3 or 4. If vinyl chloride is the compound of concern, the collision gas is set at one for maximum response. This setting reduces sensitivity to all other target compounds.
4) The source current is controlled externally and is not under computer control.
5) The optimum current for the LPCI source is source specific. It is usually set in the range of 0.010 to 0.030 microampere (µa), but can optimize around 0.075 µa. Although 0.045 µa is best for SF_6.
6) A clean source maximizes linearity and sensitivity. Paying particular attention to the high vacuum side of the LPCI source around its orifice and maintaining a high polish on that surface is of significant help.

APCI Tuning

1) The performance of the APCI source is greatly affected by both the OR and RNG values in the State file. These values are compound specific and within classes of compounds.
2) The RNG values suggested in the TAGA manual are much too high for some of the targeted compounds. The manual does not recommend using RNG values below 100 volts (V), however, diisopropylmethylphosphonate (DIMP) optimizes with a RNG value below 5V. This voltage results in the formation of large background cluster ion peaks, which do not interfere with DIMP.
3) Due to different optimum conditions required, dissimilar target compounds are unlikely to be monitored simultaneously at optimum sensitivity. Using different tune parameters for different ion pairs when creating the method can improve this situation.

Optimizing Lens Voltages

Optimization is an iterative process, with settings of one parameter affecting the optimum settings for other parameters. As the ion intensity can exhibit two or three maxima over a reasonable range of voltages, it is usually best to use the SCAN PARAMETER approach, so the operator can look at the entire voltage range at the end of the scan and base decisions on the overall picture.

1) Orifice Plate (OR) [APCI only]

The orifice plate affects the amount of declustering and fragmentation an ion will undergo in the inlet region of the interface; the higher the voltage, the greater the amount of declustering and/or fragmentation.

2) Focusing Ring (RNG) [APCI only]

The primary purpose of the focusing ring is to help focus ions through the skimmer. It also has a strong effect on the declustering/fragmentation of ions in the inlet region. While the TAGA manual recommends RNG voltages ranging from 100 to 400 V, this is intended for the relatively heavy molecules encountered in the pharmaceutical industry. Many targeted compounds evaluated so far cannot tolerate a RNG voltage above 5 to 10 V. The RNG voltage produces strong effects on the relative abundances of ion fragments, and can have an effect up to three orders of magnitude in response. During method development, it is advisable to run the RNG through a wide range of voltages to evaluate the effect.

3) High Pressure Entrance Quadrupole (Q0) also called the AC Rods.

Q0 is usually set at -5 to -10 V (in positive ion mode), and most of the other lens parameters are set relative to it. For very fragile ions, a lower Q0 may help, but IQ1, ST, and RO1 must then be reset relative to Q1, and OR, RNG and IQ2 will need to be re-optimized. As the Q0 rods get dirty, they tend to produce a concave-up curvature of the calibration curve, starting with the heavier compounds. For instance, tetrachloroethene is affected more strongly than trichloroethene.

4) Inter-Quadrupole Lens 1 (IQ1)

IQ1 will affect peak shape and sensitivity, and usually should not be changed from its previously

determined optimum relative to Q0.

5) Prefilters (Stubbies) (ST)

The prefilter affects the focusing and transmission of ions into Q1 and has little effect on peak shape. Several minima and maxima can be observed when monitoring ion signal versus ST potential. The positions of these maxima and minima are affected by both the mass and energy of the ion. Therefore, with multiple ion pairs, a compromise value is usually needed. It is recommended by Sciex that ST = Q0 -3 to -5 V in the positive ion mode.

6) First Resolving Quadrupole (RO1)

In single and MS/MS mode, RO1 is set relative to Q0 and its offset determines the ion energy in Q1 (which affects resolution and sensitivity). Increasing RO1 will usually increase the absolute signal intensity, but will also broaden peak shapes or cause significant peak splitting. It is often useful to optimize this parameter while using the Q1 READY experiment, so the peak shapes can be viewed with changing RO1.

7) Inter-Quadrupole Lens 2 (IQ2)

In single MS mode, IQ2 is mass dependent (its optimum value becomes increasingly negative with increasing m/z {positive ion mode}. When performing single MS full scan experiments, an optimum value for the entire range should be used. This is determined experimentally. When performing SIM, the optimum will be different for each ion.

In MS/MS mode, IQ2 should initially be set relative to RO2, since the voltage applied to IQ2 can introduce cross talk if it becomes more positive than RO2. In general, using IQ2 = RO2 -5V will provide good sensitivity and eliminate cross talk. If it is necessary to increase IQ2 more positive than RO2, increasing the pause time to 20 to 50 milliseconds (ms) will help minimize cross talk.

8) Collision Cell Quadrupole (RO2)

In MS/MS mode, the potential difference between RO2 and Q0 is the collision energy. When optimizing RO2, the potentials applied to IQ2, IQ3 and RO3 should be linked to RO2 to reduce cross talk and maintain proper transmission through Q3. In general, IQ2 = RO2 - 5V, IQ3 = RO2 - 20V, and RO3 = RO2 -2 to -5 V (positive ion mode).

9) Inter-Quadrupole Lens 3 (IQ3)

In single MS mode, IQ3 has no effect on peak shape or sensitivity as long as it is kept between -100 and -200 V.

In MS/MS mode, IQ3 is set relative to RO2 and its offset is dependent on the fragment ion mass. In general, IQ3 = RO2-20 to -30 V will provide good sensitivity for all fragments when acquiring MS/MS fragment ion spectra.

When performing MRM experiments, IQ3 should be ramped and optimized for best sensitivity for

each ion transition after the collision energy has been optimized.

10) Last Resolving Quadrupole (RO3)

In single MS mode, RO3 has no effect on peak shape or sensitivity as long as it is kept between -100 and -200 V.

In MS/MS mode, RO3 is set relative to RO2 and its offset determines the ion energy in Q3 which affects resolution and sensitivity of the fragment ions. In general, setting RO3 = RO2 -2 to -5 V will give reasonably good sensitivity and peak shape. Increasing RO3 will usually increase the absolute signal intensity and broaden peak shapes. In practice, we have often found that setting RO3 = RO2 -10 V works well.

11) Deflector (DF)

The deflector slowly gets dirty, and is subject to charging. When charging occurs, ions are deflected away from the multiplier, and significantly affect sensitivity. In general, the deflector should be set for -150 to -250 in positive ion mode.

12) Channel Electron Multiplier (CEM)

The CEM degrades with time and continued use and must be re-optimized periodically. In general, if an increase of 100 volts in the CEM setting results in a small increase in signal, there is no need to increase the setting. Using higher CEM settings than necessary to do the job increases the rate of deterioration.

LPCI Negative Ion Mode

When the LPCI source is in negative mode, the background Q1 spectrum shows the presence of large number of cluster ions with few related to the target compounds. So far, the only target compound-related ions seen during our current method development process are the Cl^- ions associated with chlorinated organics, and these are present in small amounts.

APCI Positive Ion Mode

The process of changing from the LPCI to the APCI source can be expected to take about an hour. This will include venting the system, changing the hardware, and pumping down. The procedures are described in Section 7.2, TAGA IIe End of Day Shut-Down and Section 7.15, changing Ionization Sources..

The APCI mode is more selective and sensitive for some compounds than the LPCI mode. For instance, the APCI lower limit of detection for pyridine is below 5 parts per trillion by volume (pptv), nearly 1000 times more sensitive than the LPCI. However, the response of the APCI is much more sensitive to inlet conditions, and the optimum conditions for one class of compounds may be very different for the optimum conditions for another class. Therefore, it is unlikely that the APCI will be used to analyze compounds of different chemical classes simultaneously.

When developing an APCI method for any compound, it is essential to first view the Q1 mass spectrum while

varying both the orifice (OR) and the ring (RNG) throughout their ranges to determine the optimum compromise among sensitivity, fragmentation and presence of background cluster ions. A detailed explanation of the effects associated with varying the controls is available in the TAGA IIe Manual.

APCI Negative Ion Mode

The APCI source in the negative ion mode has significant sensitivity for very limited classes of compounds, particularly acids. The APCI has been shown to have detection limits for organic (and volatile inorganic) acids in the low ppt range. These ions are very stable, but do not show any indication of further fracture in Q2, therefore, the ion pairs tend to be restricted to the same ion for parent and 'daughter'. This is not true for chlorine dioxide and chlorine, whose parent ions are sufficiently labile to fragment. While the selectivity is relatively great because of the very limited number of substances that respond in the negative ion mode, the specificity is very limited. For instance, it is impossible to tell isobutyric acid from butyric acid because they have the same molecular weights, and the negative ions are too stable to fragment under TAGA conditions. Therefore, while it can be ascertained that a C_4 organic acid is present; which isomer (or mix of isomers) is/are present cannot be determined.

Other than tuning parameters, the operation of the APCI is the same as the LPCI, so all of the previous operating procedures are valid. However, the high air flow precludes using the APCI mode for some sampling protocols, such as Tedlar bag sampling.

APPENDIX D
MKS 146C Cluster Gauge Controller Operation
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February 2011

MKS Model 146C Cluster Gauge Controller (Picture 11)

The MKS 146C Gauge Controller, as described in this SOP, controls the functions of the two 0 - 100 mL/min flow controllers used for controlling low flows of the standard gases and the Sample Air Flow (SAF) controller which pulls air through a Teflon hose and the glass splitters at an approximate rate of 1500 mL/sec. In addition, it controls the function of the pressure controller (0 to 10 Torr) used to control the pressure in the LPCI source.

Specifications and Environmental Limitations:

Ambient operating temperature: 59 to 104 degrees Fahrenheit (ºF). (**Note: This is a real upper temperature limit. The unit displays an error message and will no longer operate at this temperature.)**
Supply voltage fluctuation: ± 10%.
Altitude: up to 2000 meters.
Maximum relative humidity: 80% up to 31 degrees Centigrade (°C), decreasing linearly to 50% at 40°C.
Power: 100 to 120 VAC, 150VA (Watts).
Maximum potential between chassis and ground: 3.5 Volts.

Overview of Modes:

There are three standard modes for the 146 unit: Normal, Leakage, and Setup. Two additional modes are available if the optional Control board is installed: Control and Tuning. **Only the Normal and Setup modes are used in this SOP.**

Normal Mode:	The screen is not labeled.
Leakage Mode:	Displays the LEAKAGE legend.
Setup Mode:	Displays the SETUP legend.
Tuning Mode:	Displays the TUNING legend.
Control Mode:	Displays the five valve positions (OPEN, AUTO, CLOSE, HOLD, and MANUAL).

Before operating the Mass Flow Controllers:

- Check to be sure that the unit is plugged into the appropriate power supply.
- Turn on the power switch on the front of the MKS Type 146C Cluster Gauge Controller.
- Turn on power to the Sample Air Flow pump/MFC unit.
- Turn on gas supply to the Mass Flow Controller, and set at approximately 20 psig.

How to change the display of the 146 unit from one mode to another:

Use the [Display Mode] key to scroll through Normal, Leakage, Tuning and Setup Modes.
Use the [Control Mode] key to toggle in and out of Control Mode, which is not used in TAGA operations.

Overview of the Operating Modes:

Normal: This is the default mode. This is the mode for monitoring sensor readings, zeroing MFCs, and for turning MFCs on or off.

Leakage: This mode is not used in this SOP. The leakage mode is similar to the Normal mode because the same functions can be performed in both modes. However, in the leakage mode the instantaneous leakage or leakage rate (rather than pressure) is shown in the main display.

Setup: This is the mode for setting flows/pressure or for calibrating flow controllers.

Sensor Status Messages: Several control panel displays which indicate potential problems or instrument conditions are as follows:

E0:	Disconnected Sensor.
E1:	Bad Sensor
"----"	Under Range Sensor (lower segments turned on)
"----"	Over Range Sensor (upper segments turned on)
".." or "...."	Channel Turned Off
"."	Channel auto-powered off.

OPERATION:

1. <u>How to Turn On/Off an MFC</u>

   1.1. Repeatedly press the [DISPLAY MODE] key until the unit is in the Normal Mode.
   1.2. Press the [ON/LEAD] or [OFF/GAIN] key followed by [1], [2], [3], or [4] to turn the selected MFC on or off.

   Note: Channel 1 and/or 2 control the flow of standard gas into the intake manifold. Channel 3 controls the Sample Air Flow Rate. Channel 4 controls the pressure controller.

2. <u>How to Set the MFC to a Specific Flow</u>

   2.1. Repeatedly press the [DISPLAY MODE] key until the unit is in Setup Mode.
   2.2. Use the arrow keys to scroll to the CODE legend, located at lower right corner. The current control code flashes in the upper left corner of the display.
   2.3. Enter the number 17x (where x represents an MFC channel number), and press the [ENTER] key. (The standard gas feed MFC is on channel 1 and/or 2, the SAF MFC is on channel 3, and the pressure controller is on channel 4.) After pressing [ENTER], the current set point (SP) display is activated and starts flashing.
   2.4. Enter the new set point flow rate (in sccm for channel 1 and cc/sec on Channel 3), press [ENTER]. This activates the command to the MFC, setting the selected flow. (If the value to be entered is 20,000 or above, it must be entered in exponential format for the 146 unit to accept the value.)
   2.5. SP should be flashing at the upper right corner. If not, use the arrow keys to scroll through the modes of operation to SP and press [ENTER].

2.6. Press [DISPLAY] to put the unit into Normal Mode. This displays the flow rate.

Speed Note: Once in the Normal Mode and reading a flow rate, the key sequence for setting a new flow for that specific channel is: [DISPLAY MODE], [DISPLAY MODE], [ENTER], then push the number keys corresponding to the selected flow rate, [ENTER], [DISPLAY MODE].

3. How to Zero a Sensor/MFC

Before zeroing an MFC, verify that there is no gas flow through the unit. Two ways to accomplish this involve closing the upstream supply valve, or by commanding the MKS unit to close the MFC valve.

3.1. Command an MFC Close Override
- 3.1.1. Repeatedly press the [DISPLAY MODE] key until the unit is in Normal Mode (the mode in which you are reading a flow).
- 3.1.2. Press the ↓ (down arrow) key, followed by [1], [2], [3], or [4], depending on which channel you wish to close.

  The system responds by moving the MFC on the selected channel to full close within two seconds. It is best to verify zero flow with a bubble meter or other sensitive flow measurement device.

3.2. Zero the MFC
- 3.2.1. Repeatedly depress the [DISPLAY MODE] key until the unit is in the Normal Mode.
- 3.2.2. Press the [ZERO/EXP] key, followed by [1], [2], [3], or [4]. The zero value is now set.

3.3. Cancel an MFC Close Override
- 3.3.1. Repeatedly press the [DISPLAY MODE] key until the unit is in the Normal Mode.
- 3.3.2. Press the ↓ (down arrow) key, followed by [OFF/GAIN], then [1], [2], [3], or [4].

  The system responds by removing the open or close override for the MFC on the selected channel. The MFC then performs as if no override had been given, returning to the previously set flow rate.

4. How to Perform Sensor Calibration/MFC Setup (Set the Span)

At the start of each week of monitoring, it is necessary to calibrate (span) the mass flow controllers. This is done for each mass flow controller that will be used. In effect, what you are doing is changing the range of the MFC from the range indicated on the controller to one which represents its actual flow rate range. For instance, if the flow rate produced by the MFC is consistently 12% high, and the stated flow range is 100, set the flow range to 112.

4.1. Select a mass flow controller to calibrate.
4.2. If Channel 1 or 2, set the flow to 90.
4.3. If channel 3, set the flow to 1500.
4.4. Measure the selected flow with the Gillibrator for channel 1 or 2, or with the Dwyer rotameter if channel 3.
4.5. If the flow is not within 2% of the set flow, adjust the flow as follows.

4.6. Repeatedly press the [DISPLAY MODE] key until the unit is in Setup Mode.
4.7. Use the arrow keys to scroll to the SENSOR CAL legend, located at the lower right corner.
4.8. Enter a channel number in the upper left display.
4.9. Press [ENTER]. The flow range (span) for the selected MFC will flash repeatedly. (The right display will indicate FC, for mass flow controller).
4.10. Enter the new span value.
4.11. Press [ENTER]. The system responds by accepting the new value.
4.12. Re-check the flow rate, and repeat span adjustment as necessary to produce a flow within 2% of the set value.
4.13. Once the MFC has been recalibrated, verify the corrected calibration by comparing at least five set points throughout the expected operating range against a certified primary flow rate standard, such as the Gillibrator bubble meter, a DryCal unit, or against a suitable certified secondary standard. It is possible, and desirable, for the MKS unit to be calibrated be in agreement with the primary standard within one to two percent (1-2%) throughout its normal operating range as used with the TAGA.

5. Computer Interface:

The MKS Type 146 instrument is equipped with an RS-232 connector to allow computer control of the instrument. The TAGA software uses the INSTRUMENT option of the METHOD EDITOR under SAMPLE CONTROL to send control instructions to the MKS unit. The control options are in a format designed for controlling liquid chromatograph pumps. Refer to Section 7.12.2 for specific flow control instructions

The instructions for configuring the MKS Type 146 instrument so it can be controlled by the TAGA software are as follows:

5.1. Repeatedly press the [DISPLAY MODE] key until the unit is in the Setup Mode.
5.2. Repeatedly depress an arrow key until the legend “CODE” appears on the right side of the display (the number in the upper left display will be blinking).
5.3. Enter the number ‘5' in the upper left display, and then press the [ENTER] key. This will display the communication parameters, with the baud rate in the main display. It should indicate the number ‘1200'.
5.4. If the baud rate is 1200, just press [ENTER], otherwise, press the arrow keys repeatedly until the baud display indicates 1200, then press [ENTER].
5.5. The upper right display will now be flashing, and should indicate the number ‘146'. If the number ‘146' is displayed in the upper right, press the [ENTER] key, otherwise repeatedly depress an arrow key until the number ‘146' is displayed, then press [ENTER].
5.6. The upper center display should now be flashing, and it should contain the designation ‘7E’, which means seven data bits, and even parity. If ‘7E’ is in the upper center display, press [ENTER], otherwise press the number ‘7' then depress an arrow key until ‘E’ is displayed next to the ‘7', then press [ENTER].
5.7. The 146 unit can now be returned to normal operation by pressing [DISPLAY MODE] until the unit is in the normal mode, and the computer will be able to control the unit so long as the RS-232 cable is correctly attached between the computer and the 146 unit.

6. Configuring Sample Control to communicate with the MKS Mass Flow Controller.

6.1. Enter Sample Control, and select [CONFIGURATION], (Figure D.1).

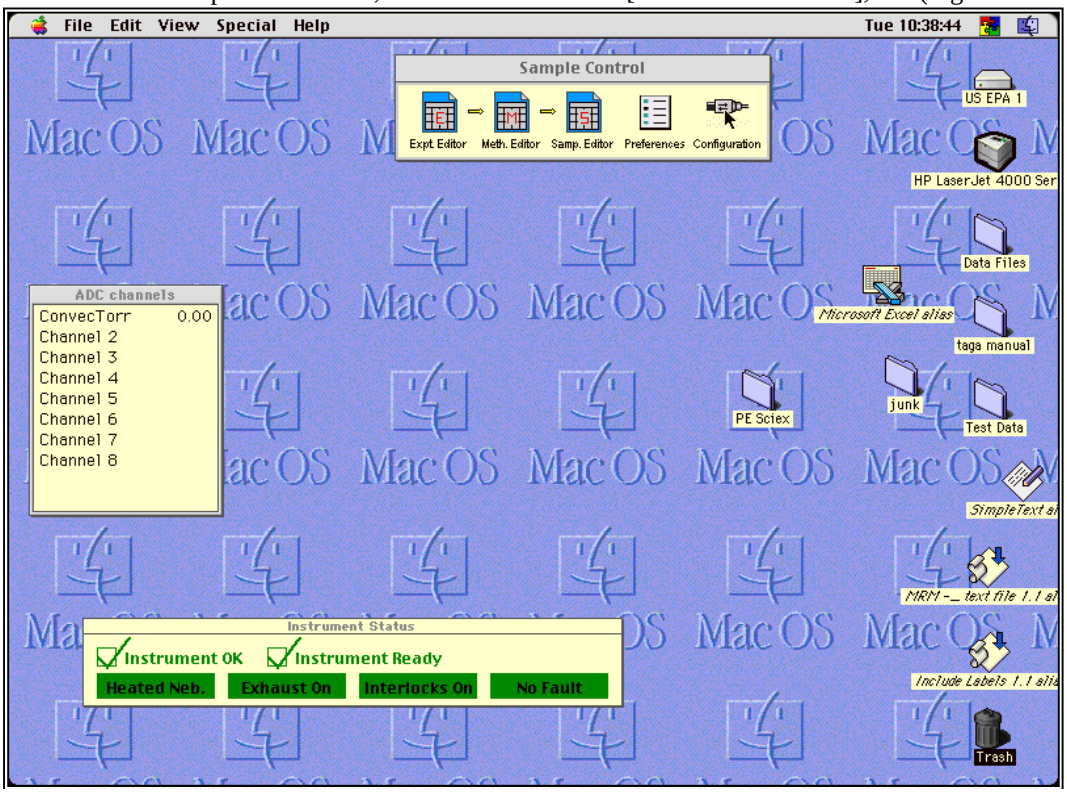

Figure D.1 Selecting Configuration

6.2. Select Channel A (Figure D.2). Note that the MKS Mass Flow Controller is physically connected to the Channel A serial port, so it must be configured on Channel A. (This was true at the time these figures were generated. However, when ECA installed the TAGAs in the buses, they added the ADC boards to the Macintosh computers, and reassigned the MKS to Channel C). In most computers, the display below will include A:, B: C: and D: as choices.

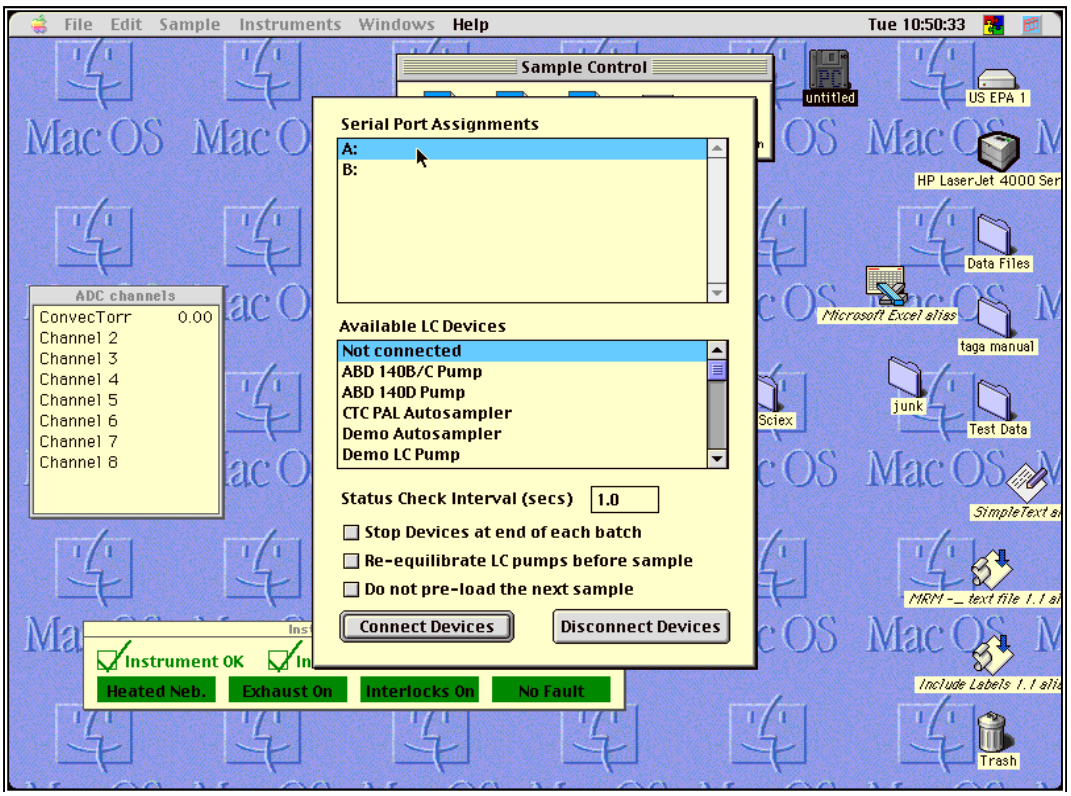

Figure D.2 Selecting Channel A

6.3. Select [MKS 146 DOUBLE] (Figure D.3). (Note: After the ECA installation in the buses, the double no longer worked, so select MKS 146 SINGLE. Either can be selected, so long as it is the same as specified in the Method under Sample Control. If they do not match, and error will be indicated when trying to load the Method, and the selection in the Method must be changed.)

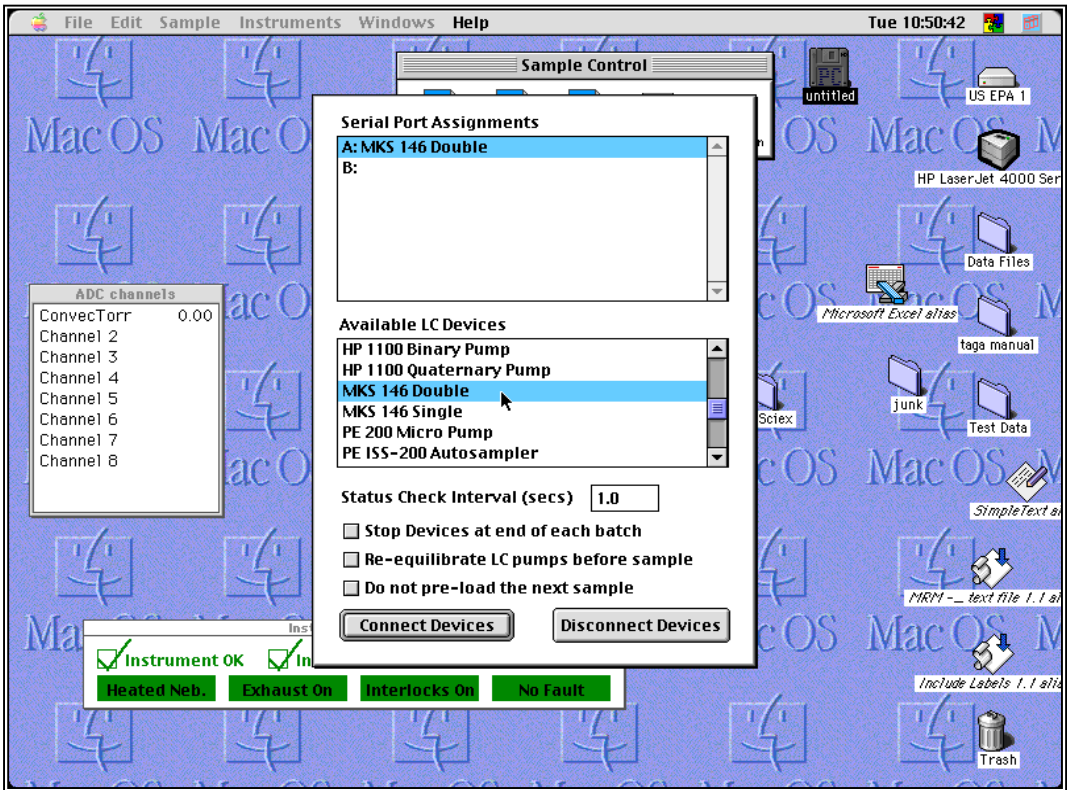

Figure D.3 Selecting the MKS Mass Flow Controller

6.4. Select [CONNECT DEVICES]. The MKS Mass Flow Controller can now be controlled by the computer.

APPENDIX E
Harvard Syringe Pump Operation
SOP #1711
February 2011

Harvard Syringe Pump

The Harvard Apparatus Syringe Pump Model 22 is designed to be operated either manually or under computer control via a standard 25-pin RS 232C connector. The Harvard Syringe Pump can make use of a wide range of syringes, with capacities from 0.5 microliter (µl) to 140 milliliter (mL), and can provide flow rates in µl/hr, µl/min, mL/hr, and mL/min. The TAGA IIe is supplied with a driver for the Harvard Syringe Pump; however, the SCIEX software makes use of only the µl/min range. In order to use any other range, the pump must be operated manually.

Temperature Controllers

A temperature controller is incorporated into the base of each Harvard syringe pump. The temperature controller is added on by SERAS staff after the temperature controller is used to control the temperature of the custom-made vaporizer (modified GC inlet) added onto the syringe pump. There are two different models of the temperature controllers in use.

1) For the model CN490 (as labeled on the front of the controller), press either the double up arrow or the double down arrow key momentarily to highlight the numerical value (set point). Press and hold either double up arrow or the double down arrow key to increase or decrease the set point. After approximately 10 seconds the unit will automatically return to reading the current temperature.

2) For the model CN9512 (as labeled on the back of the syringe pump), press and hold the star button to see the set point value. While holding the star button down use the up or down arrows to increase or decrease the set point value. The display will revert to the actual temperature value.

1 Configuring the Syringe Pump

1.1 Connect the syringe pump to the printer port of the computer using the supplied cable.
1.2 Turn on the syringe pump, and press [ENTER].
1.3 Hold the [SET] key while pressing the [STOP/START] key.
1.4 Press the [STOP/START] key until {24} is displayed.
1.5 Press [ENTER]. The syringe pump is now set for 2400 baud.
1.6 Hold the [SET] key down and press [0]. The computer displays the current address in the format AD.n, where n is the address.
1.7 Press [1], then press [ENTER].
1.8 Turn the pump's power off for two seconds, and then turn it back on. The correct address is now set.

2 Manual Operation of the Syringe Pump

2.1 Determine the syringe plunger diameter in millimeters (mm) either from the list supplied with the syringe pump or my measuring the plunger diameter. The accuracy of the flow rate depends on the accuracy of this measurement.
2.2 Depress [SET] and [DIAM] sequentially. The {mm diam} light will flash.
2.3 Using the key pad, enter the syringe diameter complete with decimal point. If you make an error, continue entering numbers until the display goes blank, and then enter the correct value.

2.4 When the display indicates the correct diameter, press [ENTER]. Note: To check the syringe diameter at any time, even while the pump is running, press [DIAM], and the diameter will appear on the display without affecting flow while the key is depressed.

2.5 Decide which range of flow rates is appropriate for use (µl/hr, µl/min, mL/hr or mL/min).

2.6 Press [SET] and [RANGE] sequentially. One of the four {Range} lights will flash.

2.7 Press [RANGE] until the correct range light is flashing.

2.8 Enter the desired flow rate, including the decimal point. If you make an error, continue entering numbers until the display goes blank, and then enter the correct value.

2.9 When the display indicates the correct rate, press [ENTER]. The display will indicate the numerical value of the rate, and the light indicating the units of flow will be on.

2.10 Be sure to set the stop collar so the syringe will be stopped before the plunger encounters the drop of liquid being used as the standard.

2.11 Start the pump by pressing [STOP/START]. The {Run} light will now be on.

2.12 To change the flow rate while the pump is running, press [SET], and [RATE] sequentially. The display will go blank, but the pump will continue running at the previously set rate.

2.13 Enter the new rate, and press [ENTER]. Once [ENTER] is pressed, the new flow rate will start.

2.14 To stop the pump, press [STOP/START]. The {Run} light will turn off.

3 Computer Controlled Operation

The Harvard Syringe Pump is controlled by the TAGA software in a manner very similar to control of the MKS Mass Flow Controller.

3.1 Turn on the power to the Syringe Pump, and press [ENTER].

3.2 Enter Sample Control on the computer, and click on Configuration (Figure E.1).

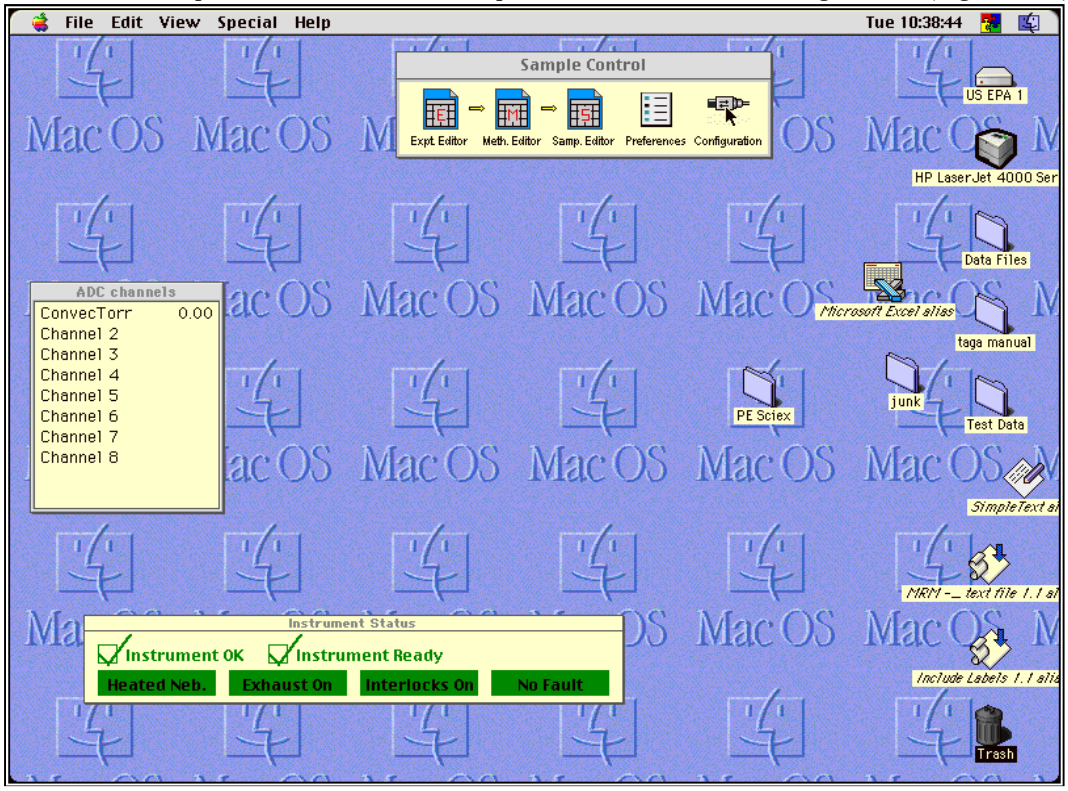

Figure E.1 Start Configuration of Syringe Pump

3.3 The Serial Port Assignments panel comes up (Figure E.3).

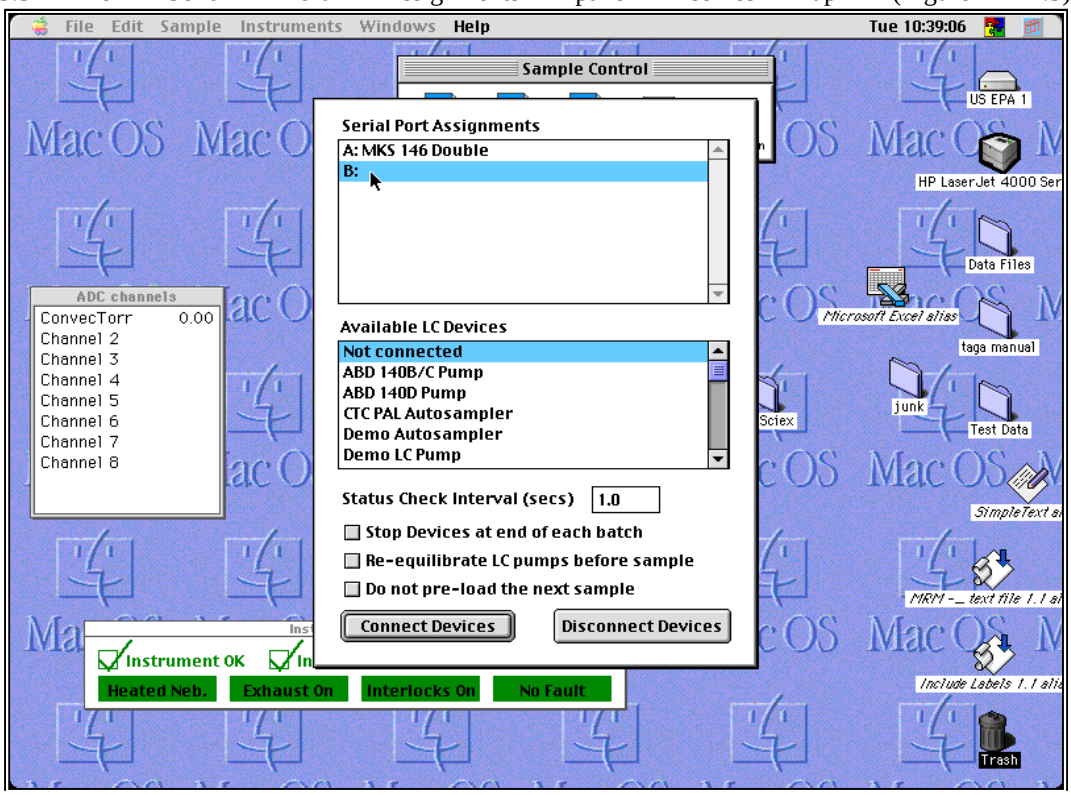

Figure E.3 Serial Port Assignment

3.4 Select the Harvard 22 Pump for channel B (Figure E.4). The syringe pump is physically connected to Channel B, so you must use that channel designation.

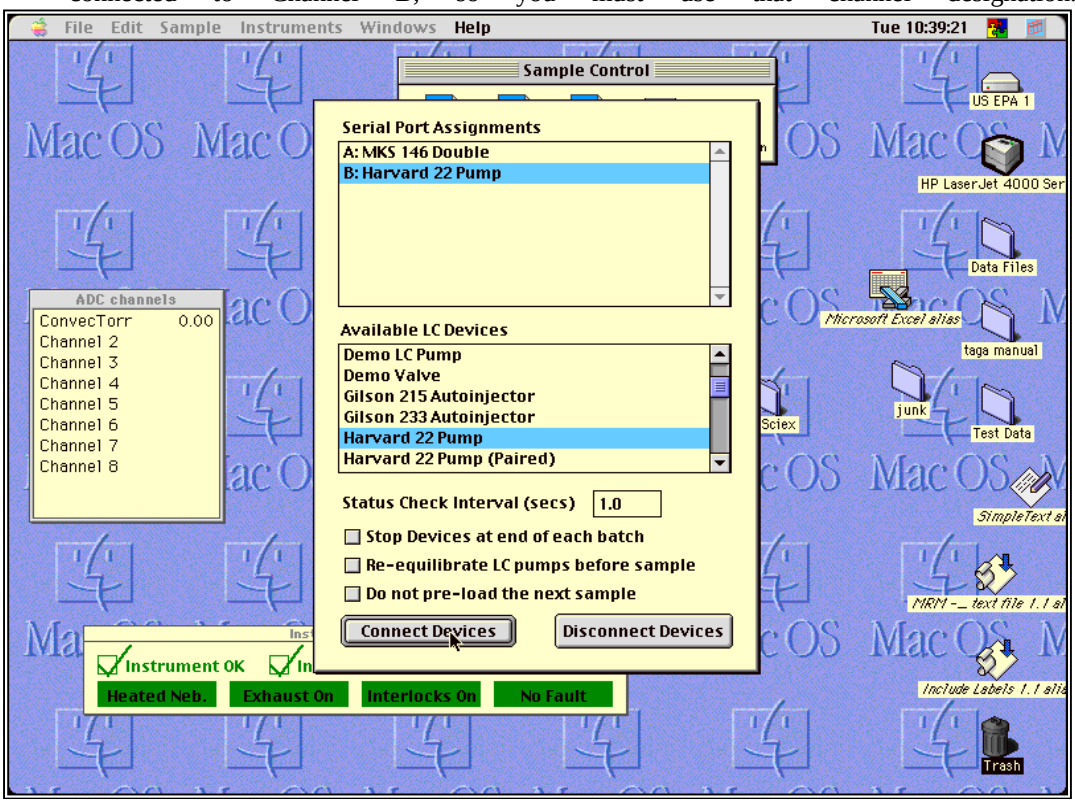

Figure E.4 Selecting Harvard 22 Pump

3.5 Click on [CONNECT DEVICES], and the computer will enable the Harvard Syringe Pump.

APPENDIX F
System File Management
SOP 1711
February 2011

System File Management

The TAGA file management system uses a specific file structure designed to maintain the integrity of the operational systems, provide logical locations for both data and user-defined operations (State, Experiment, Method, Sample, Calibration) and other files, and to minimize errors caused by the existence of multiple copies of operations files with the same name but different settings and storage locations. Each operator is assigned a specific file folder for his or her own developmental files and methods. Certain core files are "write" protected to remind each operator to make their own copies which they can modify as needed. These core files are to be copied only, no modifications can or should be done to them. Data and other task-specific files are stored by task number, with additional folders for associated calibrations and other related data.

1. Data Files

   TAGA EXPRESS stores all data files under DESKTOP: DATA. This storage location is written into the TAGA EXPRESS macro, and cannot be changed without modifying the macro.

2. Q1 and Q3 Calibration Files

   The Q1 and Q3 calibration files are stored under DESKTOP: EPA1 (or 2):INSTRUMENT: CALIBRATION. When you modify one of these calibration files under TUNE, the instrument tries to save the file under DESKTOP. In order to have the correct, modified calibration used, it must be stored in the correct location.

3. MRM TABLE

   The MRM TABLE must be located in DESKTOP: EPA1 (or 2): SYSTEM: PREFERENCES: ECAf. That is where the software looks for it. The file, MRM TABLE MASTER is the base table for any modified, job specific MRM TABLE the operator may choose to create. It may be modified only with great care.

APPENDIX G
Screen Capture
SOP #1711
February 2011

Screen Capture

The Macintosh computer allows capturing a 'picture' of the screen at any time. This is very useful in modifying or adding to the SOP.

1. To take or capture a 'picture' of the screen, hold down the [SHIFT] and [APPLE SPECIAL CONTROL] keys, and press the number [3]. This places a file, labeled 'PICTURE X' (where X is a number) in the EPA 1 (or 2) directory.
   Note: *[SHIFT] and [APPLE SPECIAL CONTROL] keys, and press the number [4] creates a picture of a rectangular portion of the screen (after pressing the keys, drag across the required section). Also, [SHIFT] and [APPLE SPECIAL CONTROL] keys, and press the number [4] and [CAPS LOCK] creates a picture of a selected pane (after pressing the keys, click on the required pane).*
2. Insert a PC formatted floppy into the Macintosh.
3. Load Microsoft Word for Windows. (Select: Apple:EPAx:Microsoft Office 98:Microsoft Word)
4. Select [INSERT], [PICTURE], [FROM FILE], and left click the mouse (Figure G.1).

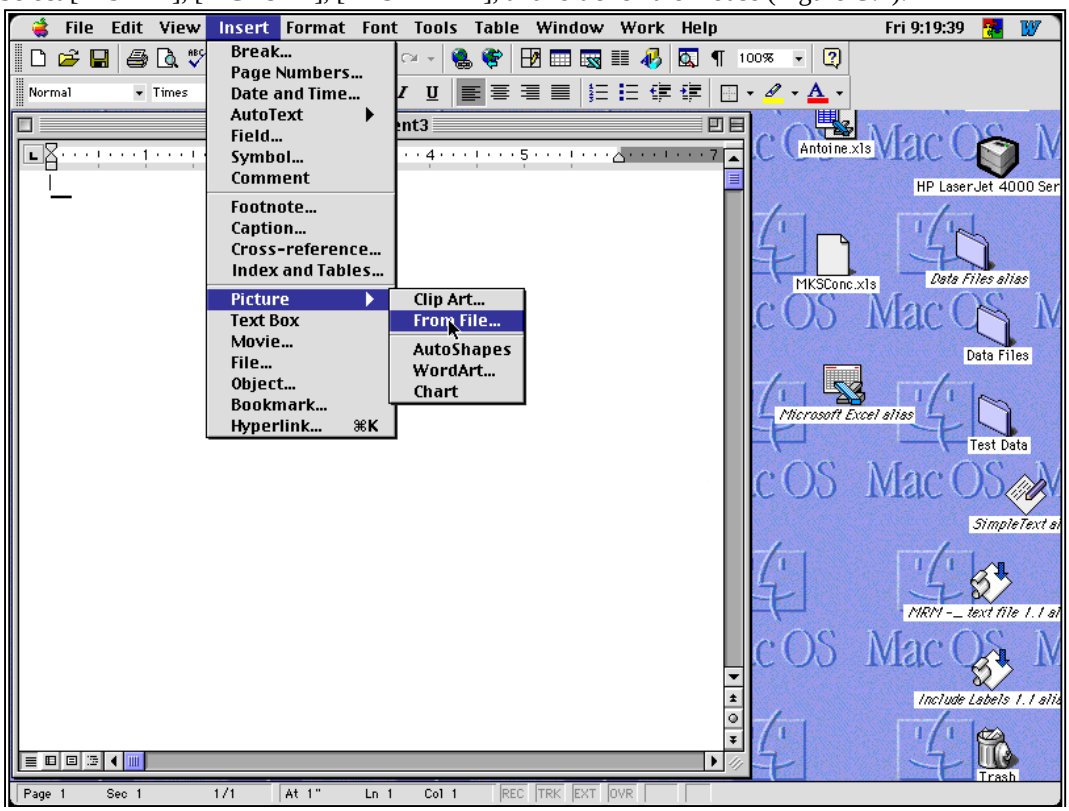

Figure G.1 Inserting Picture into Microsoft Word

5. Select the Picture file, and double click.
6. The picture will be displayed in the document.
7. Select [FILE], [SAVE AS]
8. Save the file on the floppy. Note that you will have to select a file name.

9. Remove the floppy from the Macintosh (drag the floppy's image to the trash), and take it to and insert into the PC.

APPENDIX H
Chlorine and Chlorine Dioxide
SOP #1711
February 2011

Chlorine and Chlorine Dioxide

Chlorine dioxide is used to fumigate structures contaminated with anthrax or mold. Chlorine dioxide decomposes in sunlight to form chlorine. The half life of chlorine dioxide in bright sunlight is approximately 3.5 seconds. The TAGA has proven to be the most sensitive method for monitoring chlorine dioxide, with a detection limit well below 5 parts per trillion by volume (pptv).

1. Certification of Standards
   Chlorine gas standards are generally considered stabile for approximately six months. Therefore, it is necessary to recertify the gas standards every six months, or before each job, whichever is longer.

   1.1. Certification of 50 part per million by volume (ppmv) chlorine (Cl_2) Standard – Required Every Six Months

   1.1.1. Make sure you have fresh thiosulfate and starch indicator before starting. You will need 0.0100 N sodium thiosulfate (certified VWR VW3256-1 or equivalent), 2% starch indicator, 0.1 N (VWR VW3638 or equivalent), 2% weight by volume (w/v) potassium iodide (KI) solution (VWR VW3909-1 or equivalent), and glacial acetic acid.

   1.1.2. Set up the apparatus (Figure H1) to bubble the Cl_2 standard through approximately 100 milliliter (mL) of acidified (a few drops glacial acetic acid) KI solution in a 250 mL bubbler, making sure to use a 1-liter per minute (L/min) corrosive service mass flow controller (MFC) (MKS Model 1479).

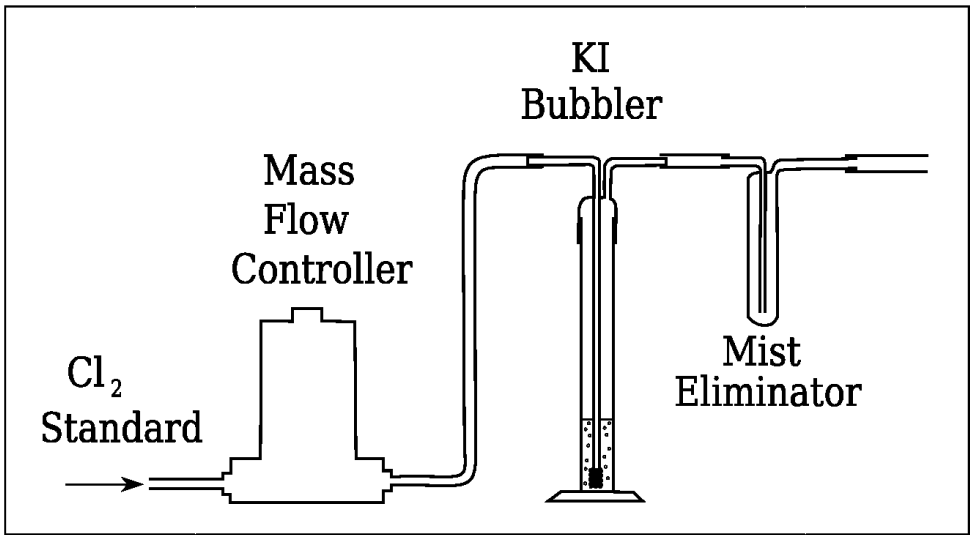

Figure H1 Chlorine Standard Certification Apparatus

   1.1.3. Before attaching the MFC exit line to the bubbler, set the standard flow to approximately 1 L/min and measure the flow accurately with a Gillibrator bubble meter, taking an average of ten measurements.

   1.1.4. Connect the standard flow to the bubbler, noting the time or starting a stop watch. You will need to measure the duration of time during which the gas is flowing through the bubbler, so use

a stopwatch, or a watch with a sweep second hand. The total time will be about 90 minutes.

1.1.5. At the end of approximately 90-minutes, note the exact time as you disconnect the line from the bubbler. Then again check the flow ten times using the Gillibrator bubble meter.

1.1.6. Quantitatively transfer the KI solution (which will now be stained with iodine) to an appropriate Erlenmeyer flask for titration.

1.1.7. Fill a burette with the 0.0100 N sodium thiosulfate solution.

1.1.8. Start titrating the KI solution using the 0.0100 N sodium thiosulfate solution, and continue until the KI solution is a pale straw color. Then add two or three drops of starch indicator. Titrate until the blue color just disappears. Record the total titration volume.

1.1.9. Use the Excel spreadsheet "Cl2CalLow". This spreadsheet can be found in the shared drive: I:\TAGA\Libraries|Calculation Aids. In the spreadsheet fill in the average flow rate, total titration time in minutes, and total titration volume in mL, creating a standard certification document (Figure H2) as shown below.

1.1.10. The operator enters into the spreadsheet into the appropriate cells: the average flow rate in mL/min, the time in minutes during which the chlorine standard is flowing through the bubbler, the mL of thiosulfate needed to titrate the blank, the mL of thiosulfate to titrate the contents of the bubbler once collection has been completed, the normality of the standard thiosulfate solution, and the temperature of the room in degrees Kelvin (ºK).

1.1.11. The spreadsheet performs the following calculations:

gas volume in mL = (Flow rate in mL/min) x (Time in min)

wt Cl2 (in mg) = (mL titration - mL blank) x (normality) x (35.45)

Moles Cl2 = (wt Cl2 in mg) / (1000) / (70.905)

Volume Cl2 in mL = (Moles Cl2) x ((Temperature) / (273.15)) x (22.414) x (1000)

Conc. Cl2 in ppmv = ((mL Volume Cl2) / (mL gas volume)) x (1,000,000)

1.1.12. The concentration of chlorine in ppmv is the concentration entered on the cylinder tag as the newly certified value.

Cl2CalLow Excel Spreadsheet

2/23/2007			Calibration of Chlorine				
	Avg. flow rate =	1004	mL/min		Time =	88	min.
	gas volume =	88352	mL				
	titration =	32.8	mL		Temperature =	298	deg K
	blank =	0	mL				
thiosulfate	normality =	0.0100	N				
	wt Cl2 =	11.6276	mg		Moles Cl2 =	1.640E-04	
Note: 35.45 is the number of grams Cl2 per							
	equivalent. The Cl goes from a 0				Volume Cl2 =	4.010	mL
	oxidation state to -1, a change of 1						
	per chlorine atom, or two per molecule.						
					Conc. Cl2 =	45.39	ppmv

SO Number:	188488
Lot Number:	102-26-03973
Cylinder Number:	AS53312
Analyst's Name:	Scott J. Thompson
Recertification Date:	2/23/2007
Expiration Date	8/23/2007
Chlorine	45.39
Balance Nitrogen	

Figure H2 Standard Certification Document for Chlorine

1.2. Chlorine Dioxide Certification – Done Once for Each New Bubbler

1.2.1. Make sure you have fresh sodium thiosulfate and soluble starch indicator before starting. You will need 0.0100 N sodium thiosulfate (certified VWR VW3256-1 or equivalent), 2% starch indicator, 0.1 N (VWR VW3638 or equivalent), 2% w/v KI solution (VWR VW3909-1 or equivalent), and glacial acetic acid.

1.2.2. Set up the apparatus to bubble standard Cl_2 through the apparatus shown below in Figure H3. The first bubbler contains a solution of 16 grams of sodium chlorite ($NaClO_2$) solid dissolved into 100 mL of deionized water. Chlorine gas bubbled through the solution is partially converted into chlorine dioxide, although all of the chlorine is consumed in the process (TAGA tests have indicated less than 0.1% of the chlorine passes through the bubbler). A small mist eliminator follows the first bubbler. The second bubbler contains acidified KI solution as used for the chlorine calibration.

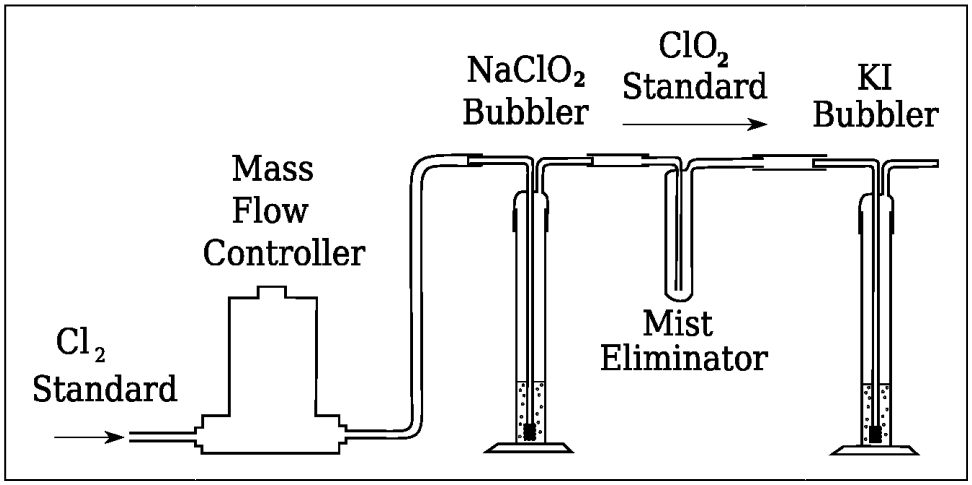

Figure H3 Chlorine Dioxide Certification Apparatus

1.2.3. Before attaching the MFC exit line to the bubbler, set the standard flow to approximately 90 mL/min and measure the flow accurately with a Gillibrator bubble meter, taking an average of ten measurements.

1.2.4. Connect the standard flow to the bubbler, noting the time or starting a stop watch. You will need to measure the duration of time during which the gas is flowing through the bubbler, so use a stopwatch, or a watch with a sweep second hand. The total time of collection will be about 180 minutes.

1.2.5. At the end of approximately 180-minutes, note the exact time as you disconnect the line from the bubbler. Again check the flow ten times using the Gillibrator bubble meter.

1.2.6. Quantatively transfer the KI solution (which will now be stained with iodine) to an appropriate erlenmeyer flask for titration.

1.2.7. Fill a burette with the 0.0100 N sodium thiosulfate solution.

1.2.8. Start titrating the KI solution using the 0.0100 N sodium thiosulfate solution, and continue until the KI solution is a pale straw color. Then add two or three drops of starch indicator. Titrate until the blue color just disappears. Record the total titration volume.

1.2.9. Use the Excel spreadsheet "ClO2CalLow" in the Calculation Aids folder in the shared drive, under TAGA, Libraries, filling in the average flow rate, time in minutes, and titration volume in mL, as shown in the figure below (Figure H4).

ClO2CalLow Spreadsheet

			Calibration of Chlorine Dioxide				
	Avg. flow rate =	90	mL/min		Time =	201	min.
	gas volume =	18090	mL				
	titration =	21.65	mL		Temperature =	298	deg K
	blank =	0	mL				
thiosulfate	normality =	0.01	N				
	wt ClO2 =	2.920585	mg		Moles ClO2 =	4.329E-05	
Note: 13.49 is the number of grams ClO2 per							
	equivalent. The Cl goes from a +4				Volume ClO2 =	1.059	mL
	oxidation state to -1, a change of 5.						
					Conc. ClO2 =	58.52	ppmv

Figure H4 Standard Certification Document for Chlorine Dioxide

1.2.10. The operator enters the average flow rate in mL/min, and the time in minutes during which the chlorine standard is flowing through the bubbler, the mL of thiosulfate needed to titrate the blank, the mL of thiosulfate to titrate the contents of the bubbler once collection has been completed, waiting at least five minutes after the flow has stopped for the reaction to be complete, the normality of the standard thiosulfate solution, and the temperature of the room in ^{o}K.

1.2.11. The spreadsheet performs the following calculations:

$$\text{gas volume in mL} = (\text{Flow rate in mL/min}) \text{ x } (\text{Time in min})$$

$$\text{wt ClO2 in mg} = ((\text{mL titration}) - (\text{mL blank})) \text{ x } (\text{normality}) \text{ x } (13.49)$$

$$\text{Moles ClO2} = (\text{mg ClO2}) / (1000) / (67.46)$$

$$\text{Volume ClO2 in mL} = (\text{Moles ClO2}) \text{ x } ((\text{Temperature}) / (273.15)) \text{ x } (22.414) \text{ x } (1000)$$

$$\text{Conc. ClO2 in ppmv} = ((\text{mL Volume Cl2})/(\text{mL gas volume})) \text{ x } (1{,}000{,}000)$$

1.2.12. The concentration of chlorine dioxide in ppmv is the concentration produced when the chlorine standard is passed through the sodium chlorite bubbler. The concentration of chlorine dioxide produced is divided by the concentration of chlorine provided. The ratio usually ranges from 1.27 to 1.29. The bubblers most commonly used for this process have produced a ratio of 1.29. Therefore, when using the set-up specified herein, use 1.29 times the certified chlorine concentration as the 'tank' concentration of the chlorine dioxide when producing the TAGA concentration table (see below).

1.3. After certifying the chlorine concentration in the standard cylinder, and recertifying the conversion factor to chlorine dioxide if necessary, be sure to make the appropriate changes in the concentration tables in the TAGA computer. Several of the cylinder spreadsheets under Calculation Aids incorporate calculation of the chlorine and chlorine dioxide concentrations. Enter the cylinder concentration of chlorine where indicated. Most of the spreadsheets automatically multiply the chlorine value by 1.29 for the chlorine dioxide concentration. Verify the ratio to be sure it is correct for the type of bubbler in use. Measure the SAF flow into the source. It is very common for the APCI inlet flow to be around 1200 cc/sec when the SAF controller flow is 1500 cc/sec. The APCI source is not sealed. Once the chlorine and chlorine dioxide concentrations are correctly entered, and the correct, measured inlet flow is used, the correct concentrations are displayed in parts per trillion by volume (pptv) in the lower section of the spreadsheet. Copy and "Paste Special" the values from the cylinder spreadsheet into the appropriate concentration table in EPA2:System:Preferences:ECAf:Concentrations.

2. Tuning for Chlorine and Chlorine Dioxide

This section describes the basic procedure for tuning the TAGA for both sensitive and reasonably stabile monitoring of chlorine dioxide and chlorine. It is assumed that the operator is thoroughly familiar with the body of the SOP, and this section addresses only those specifics which are different or particularly notable.

2.3. Equipment set-up.

2.3.1. Install the APCI ionization source, and be sure the gold needle is used, and is placed near the edge of the air stream entering the source.

2.3.2. Set up the chlorine and chlorine dioxide standard introduction system as shown in Figure H5, to allow both gases to be introduced into the sample stream simultaneously. Start the SAF, and start the gases flowing. It usually takes a fresh $NaClO_2$ bubbler about 30-minutes to reach constant output. That is because the chlorine dioxide is highly soluble in water. More rapid equilibrium may be reached by preparing the stock sodium chlorite solution in a polypropylene bottle, and putting an appropriate amount into a smog bubbler, which uses much less solution.

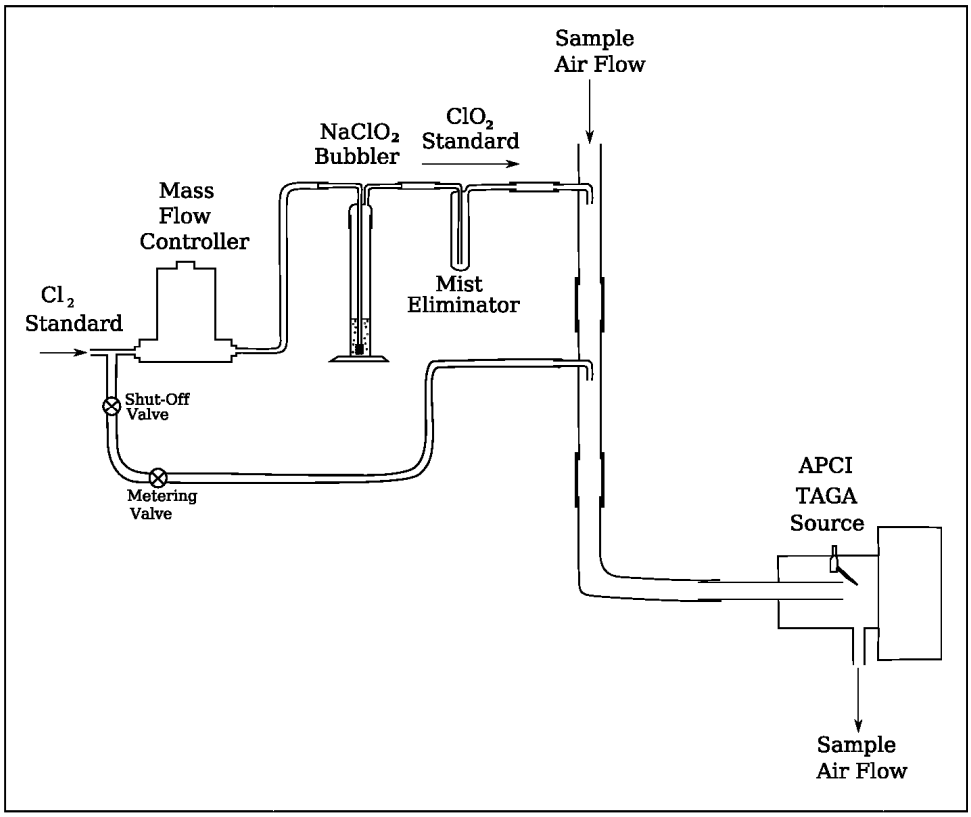

Figure H5 Chlorine and Chlorine Dioxide Tuning Setup

2.3.3. Load an experiment file incorporating the ion pairs listed below (i.e. Neg Cl2 + ClO2 Mob). Note: it is important to be sure that if a new Experiment is created, the Q2 Purge is off.

Ion Pairs for Chlorine and Chlorine Dioxide

Compound	Parent Ion Mass	Daughter Ion Mass
Chlorine Dioxide	67	51
Chlorine Dioxide	69	53
Chlorine	70	35
Chlorine	72	37
Chlorine	72	35

2.3.4. Load the most recent State file used for chlorine and chlorine dioxide. The state file name usually incorporates the terms, “Neg APCI”. Then select the calibrations, “Negative APCI Q1” and Negative APCI Q3”. A typical state file used for monitoring during a chlorine dioxide decontamination event is as follows:

2.3.5.

Typical State File:
Negative Ions
Gases

CUR	9
CAD	2

Controls

NC	-2.0
TEM	0.0
OR	-15.0
RNG	-80.0
Q0	6.0
IQ1	8.0
ST	11.0
RO1	8.6
IQ2	14.5
RO2	23.0
IQ3	28.2
RO3	32.0
DF	180
CEM	2000

2.3.6. Tune the instrument to give the best response to ClO_2, while maintaining reasonable response to Cl_2.

2.3.7. Once the basic tuning for the target substances has been completed, adjust the mass assignment and peak width using a pre-prepared mixture of organic acids, designated “MA”. The mixture includes organic acids from C3 through C9, and has the relative amounts are selected by the operator to provide approximately equal vapor pressures.

2.3.8. Select a small screw-cap ampoule labeled, “MA”, and place it, with a slightly loosened cap, into an apparatus at the inlet of the APCI source, arranged as shown in Figure H6.

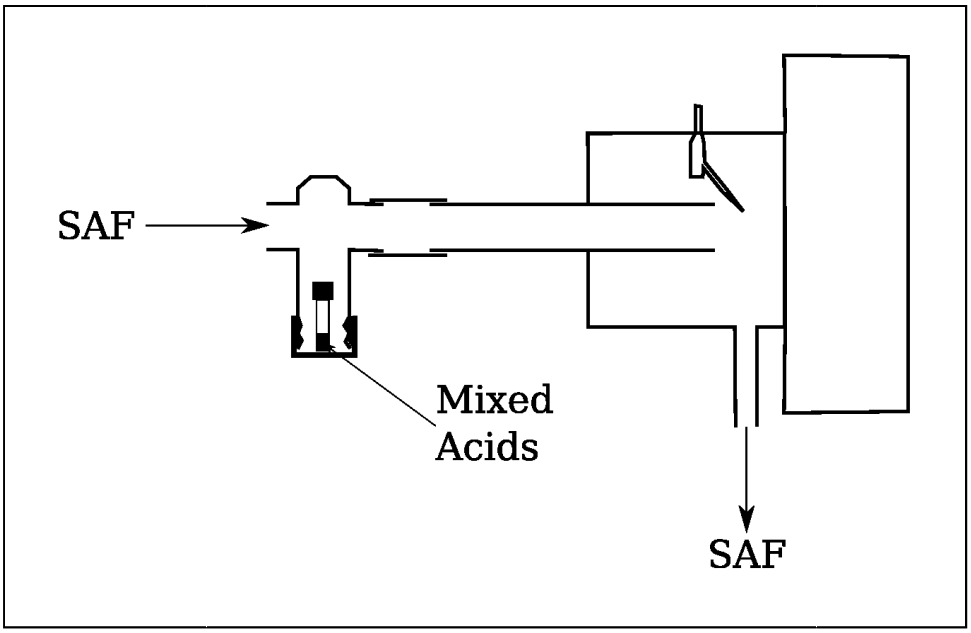

Figure H6 Apparatus for Introducing Mixed Acids

2.3.8.1. Adjust the Q1 and Q3 peak widths in the same manner as is done for the LPCI. This is discussed in detail in section 7.4, Mass Calibration, of this SOP. The experiment files to be used are as follows; "MIXED ACIDS NEG Q1", and "MIXED ACIDS NEG Q3". Also select the "MIXED ACIDS" Reference File in the Reference window.

2.3.8.2. The exact masses used for this tuning are the same for both Q1 and Q3, and the masses are: 73.03, 87.04, 115.08, 129.09, 143.11, and 157.12, corresponding to parent ions from propionic acid, butyric acid, hexanoic acid, heptanoic acid, octanoic acid, and nonanoic acid. Since monitoring is in negative ion mode, these masses, minus one hydrogen atom, represent the molecular ions of each compound within the mixture of organic acids.

2.3.8.3. Once the peak widths are satisfactory, if the delta mass assignments differ by more than 0.05 mass units, click "Replace", and save the new Q1 or Q3 calibration into the EPA2:Instrument:Calibration folder.

2.3.8.4. Remove the Mixed Acids apparatus from the APCI, and replace it with the set-up used to tune for chlorine dioxide and chlorine as shown above.

2.3.9. Re-evaluate the tune for the target substances, and modify slightly if necessary. If significant changes are made, you will need to re-test the peak widths and mass assignment again.

2.4. Calibrating the TAGA for Chlorine and Chlorine Dioxide.

While adding chlorine to a stream of chlorine dioxide does not appear to cause an appreciable decrease in the TAGA's response to chlorine dioxide, the reverse is not true. Adding a stream of chlorine dioxide to a stream of chlorine can cause a depression of up to 25% in the TAGA's response to chlorine. Therefore, the two substances are calibrated separately.

2.4.1. Calibrating the TAGA for chlorine.

2.4.1.1. Since equilibration of the chlorine dioxide generator can take up to 30-minutes, the chlorine is calibrated first, while the chlorine dioxide generator is equilibrating. Set up the equipment as shown in Figure H7.

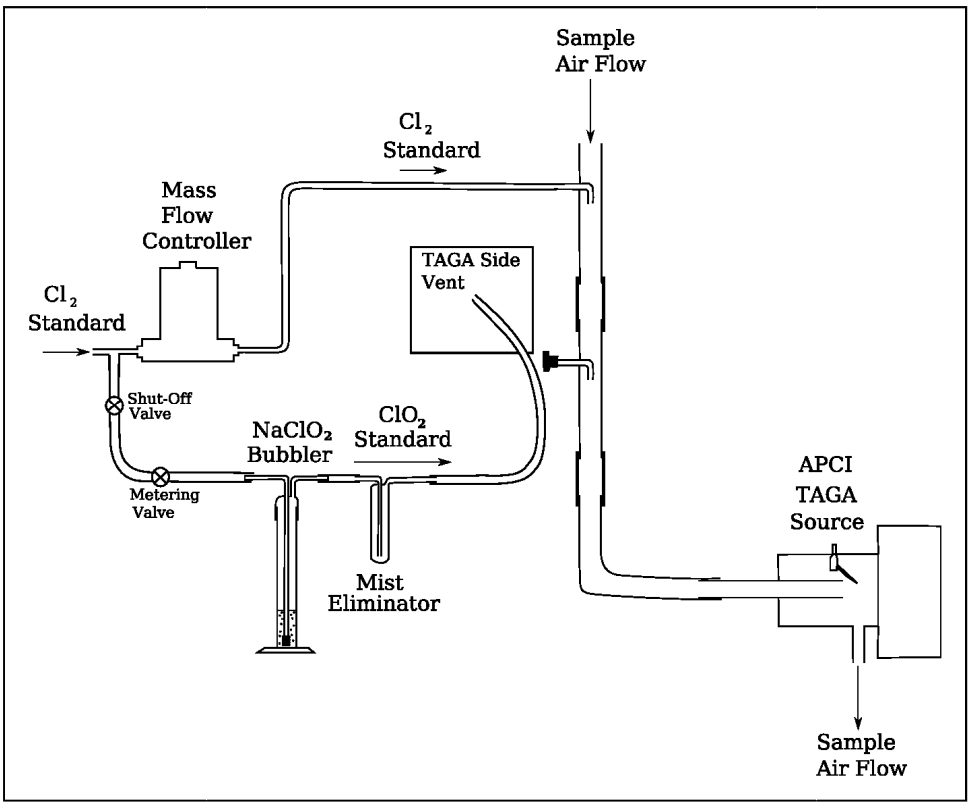

Figure H7 Chlorine Calibration Set-Up

2.4.1.2. After exiting Tune, Load TAGA Express.

2.4.1.3. Make sure the Method file for the chlorine calibration, Cl2 Calibration, has been updated to reflect the current state file.

2.4.1.4. Run the Cl2 Calibration method and acquire the Cl2 calibration data.

2.4.1.5. Once the acquisition is complete, make sure Excel had been loaded, and click the script at the top of Multiview, and select Create Calibration. Then proceed as with any other TAGA calibration (see the TAGA SOP, Section 7.6).

2.4.2. Calibrating the TAGA for chlorine dioxide.

2.4.2.1. Set up the equipment as shown in Figure H8.

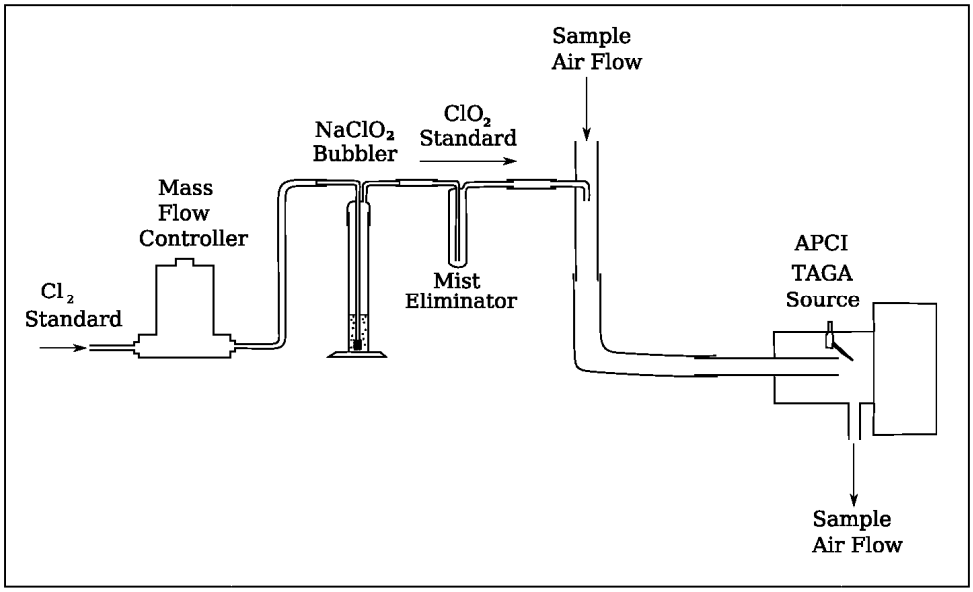

Figure H8 Chlorine Dioxide Calibration Set-Up

2.4.2.2. The chlorine dioxide calibration proceeds most smoothly if the concentrations are introduced from highest to lowest, so be sure the concentrations are introduced in that order.

2.4.2.3. Chlorine dioxide is very reactive, so try to avoid being down-wind of engine exhaust of any type. The presence of exhaust gases will cause severe dips in the chlorine dioxide concentration in the gas stream.

2.4.2.4. Run ClO2 Calibration method and acquire the ClO2 calibration data.

2.4.2.5. Once the acquisition is complete, make sure Excel had been loaded, and click the script at the top of Multiview, and select Create Calibration. Then proceed as with any other TAGA calibration (see the TAGA SOP, Section 7.6).