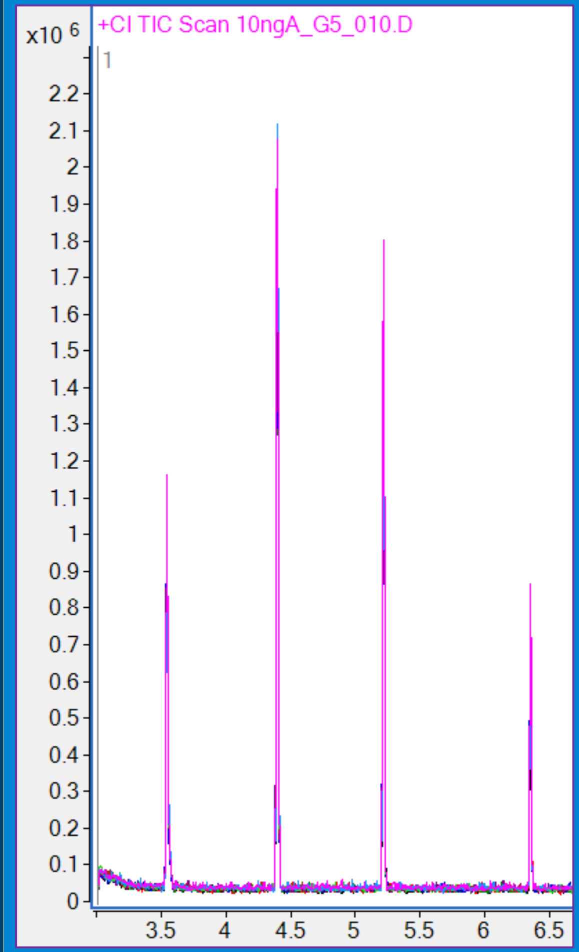
5977 Chemical Ionization



DE44308.5415625

Chemical Ionization:

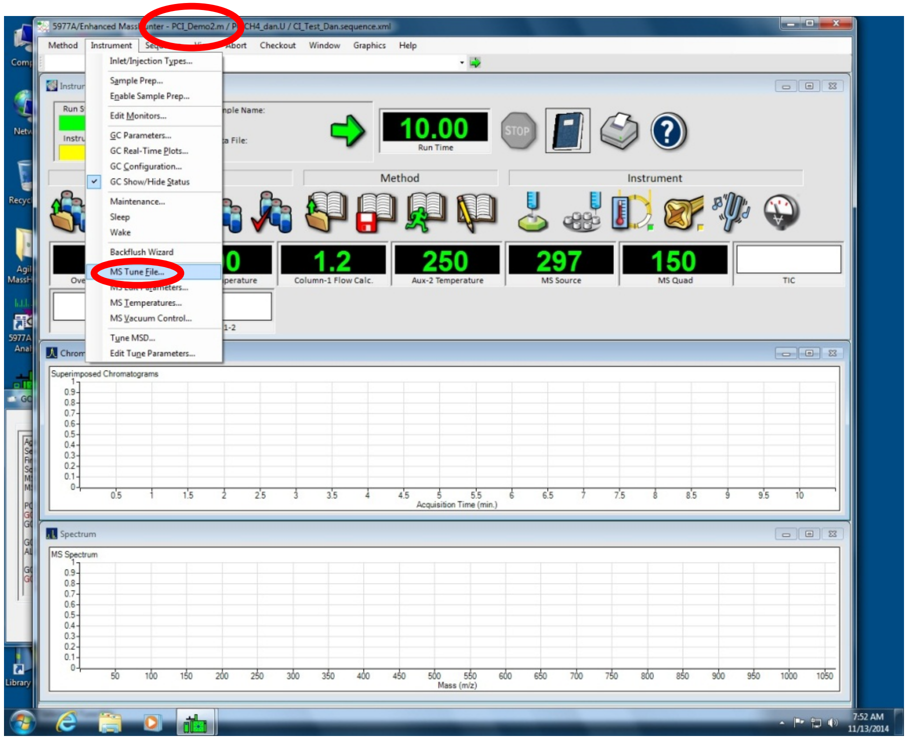
For theory of operation, see the Concept Guide for the specific GCMS system

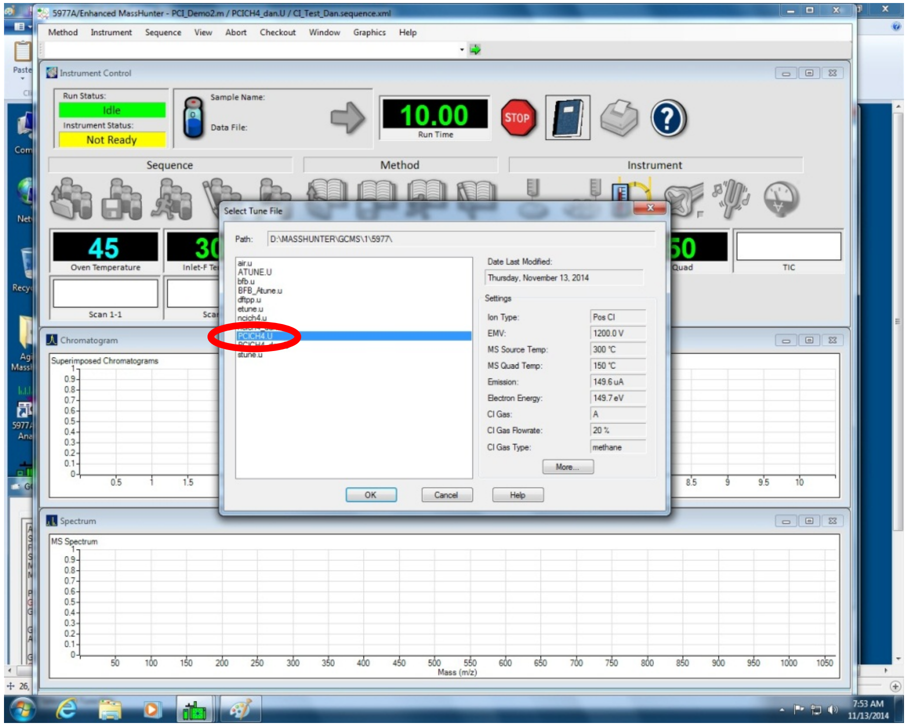
PCI
- Proton transfer
- Hydride abstraction
- Addition
- Charge exchange

NCI
- Electron capture
- Dissociative electron capture
- Ion pair formation
- Ion-molecule reactions

Chemical Ionization: Load the PCI Checkout method and then select the default tune file

This is not the correct name…





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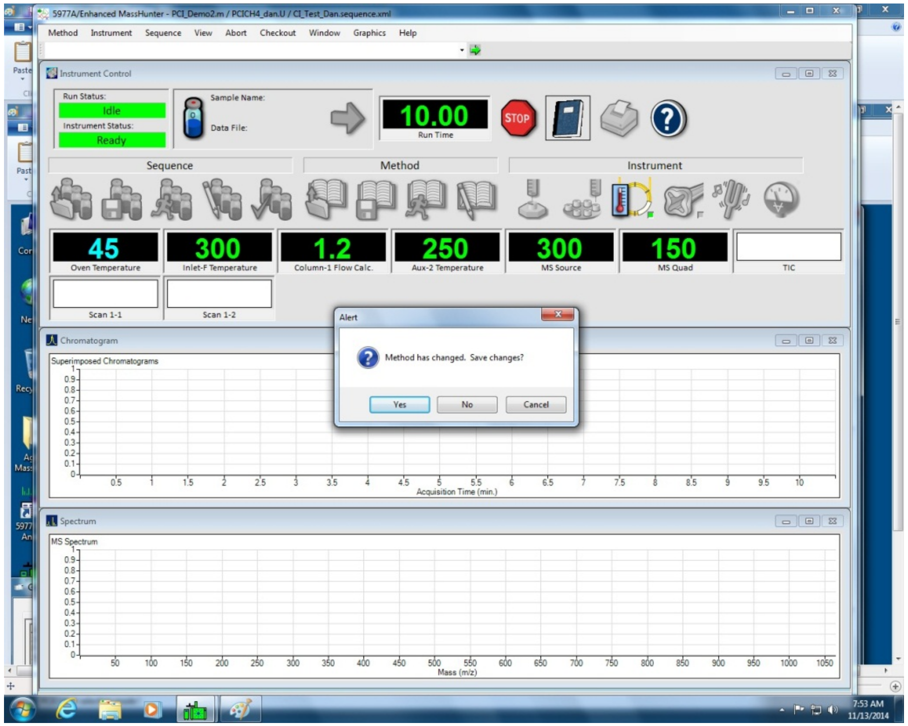
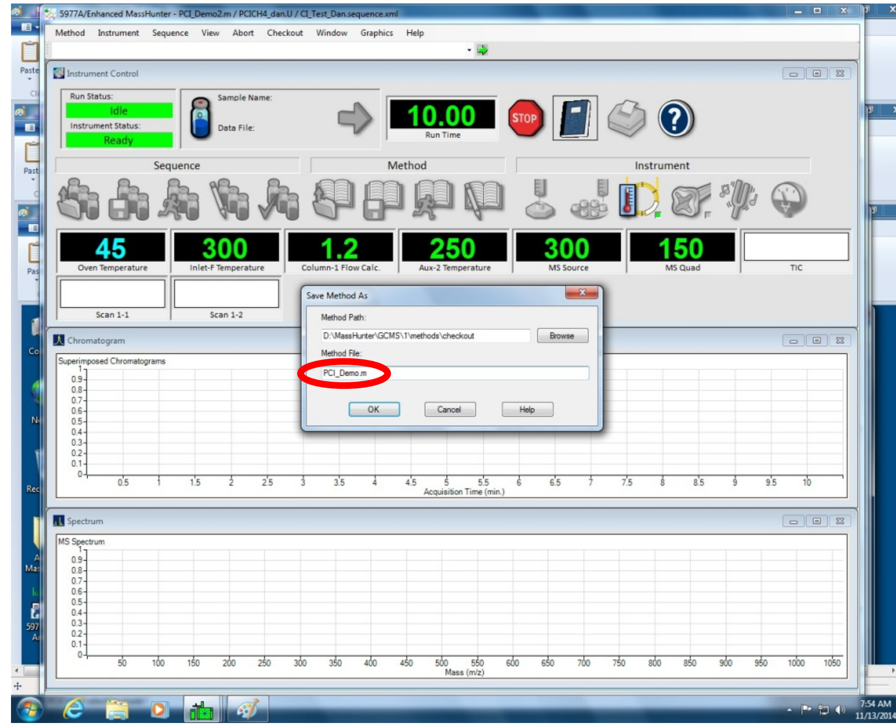
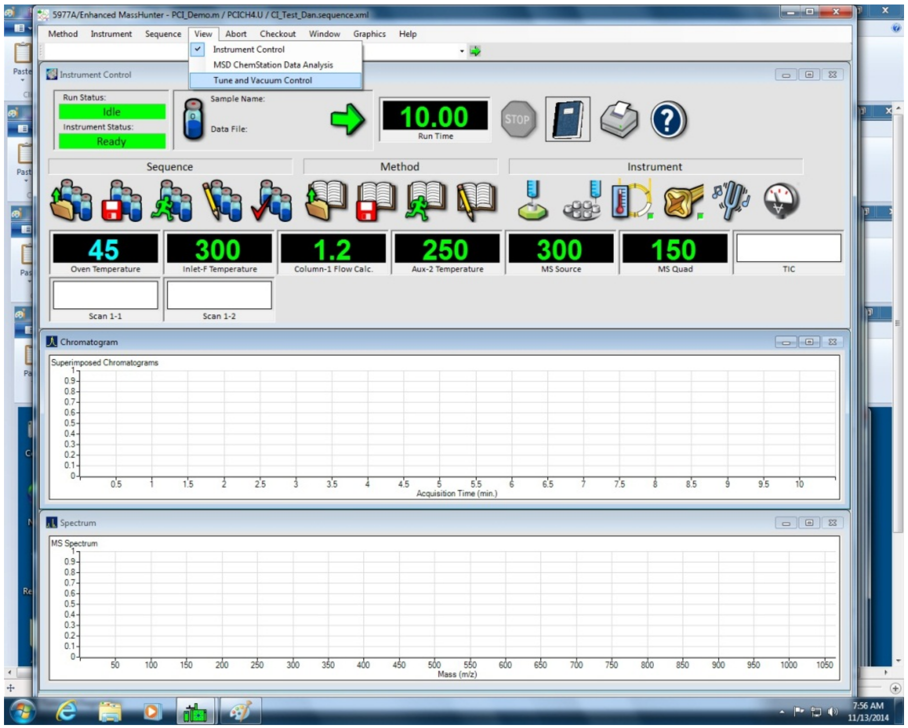
Chemical Ionization: Load the PCI Checkout method and then select the default tune file

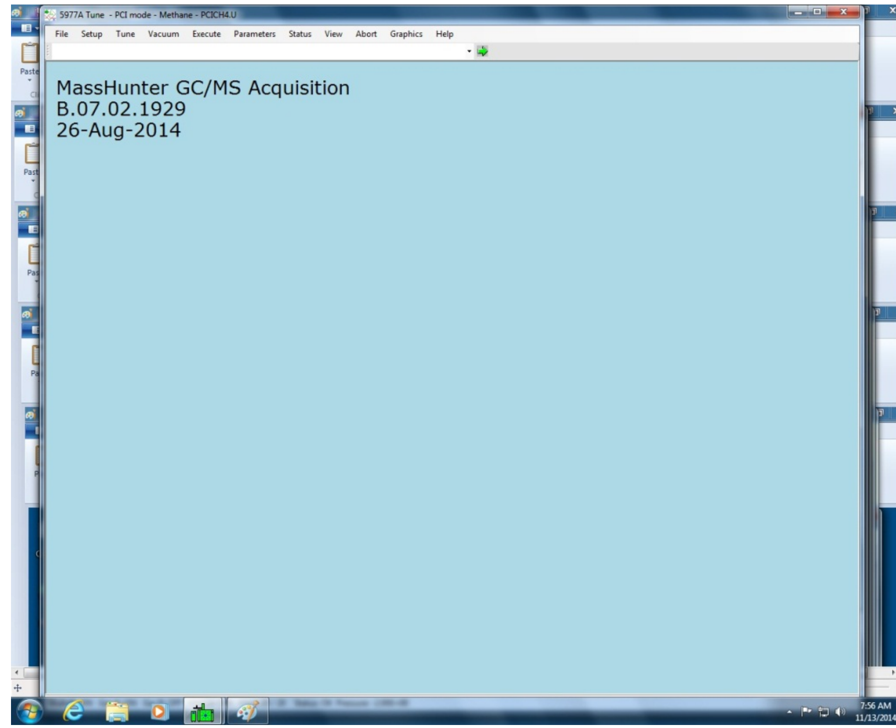




Do not save over the checkout method! Name it something like PCI_USxxxxxxxx.M with the Xs being the instrument serial number

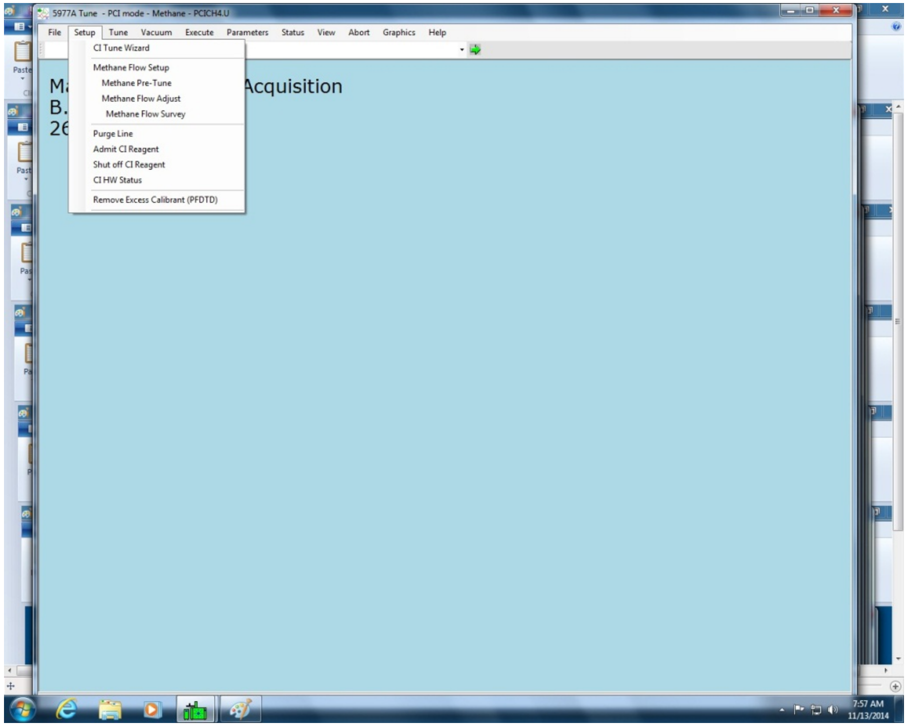
Chemical Ionization: Load the PCI Checkout method and then select the default tune file

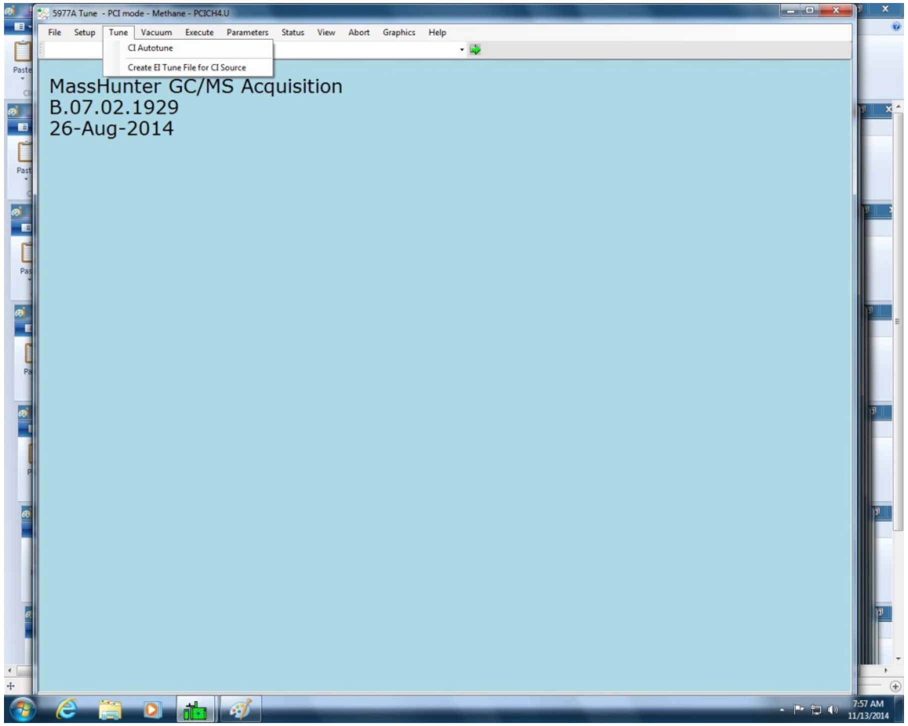




Agilent

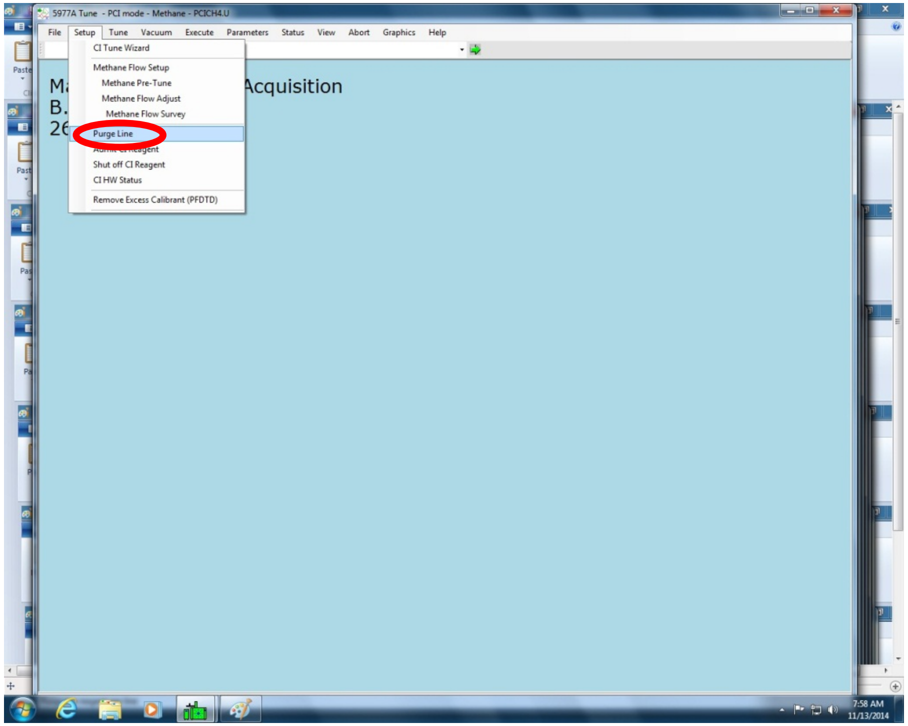
Chemical Ionization: Load the PCI Checkout method and then select the default tune file

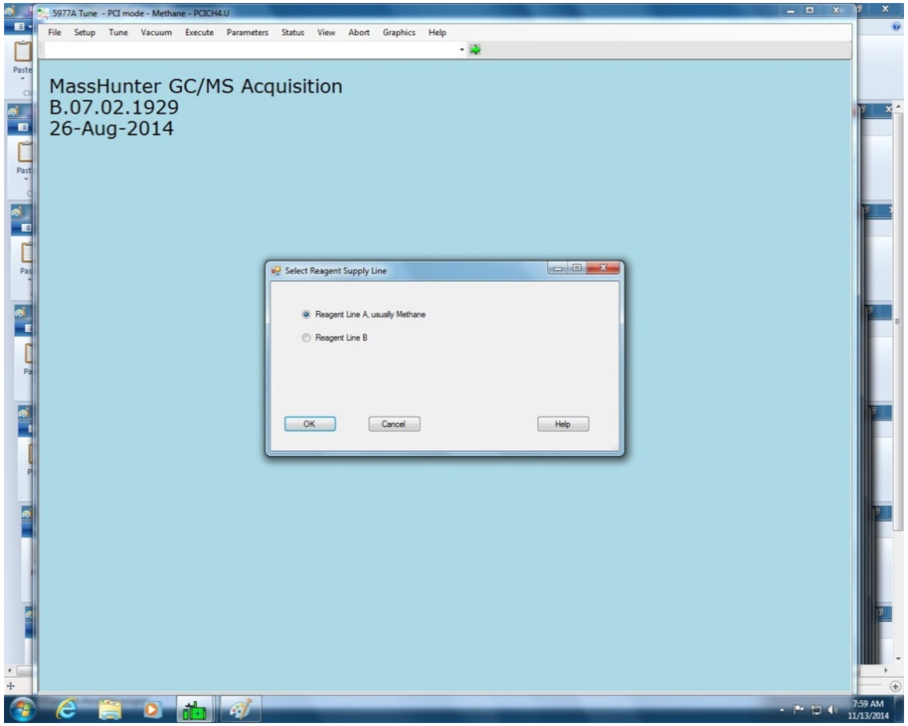




These two screen captures show the menus available when PCI is selected.

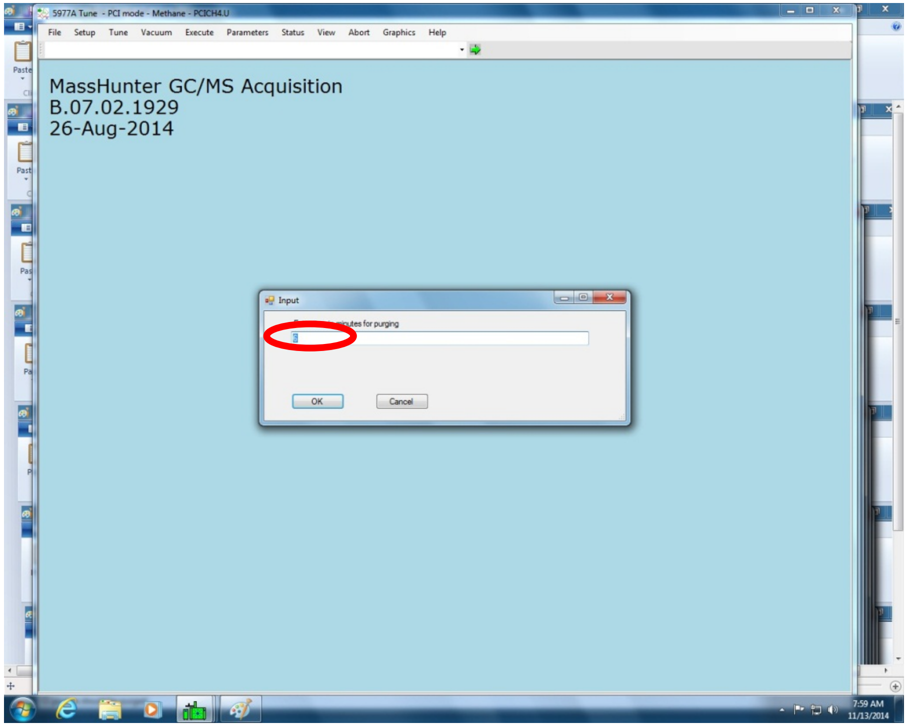
Chemical Ionization: Purge the methane gas line



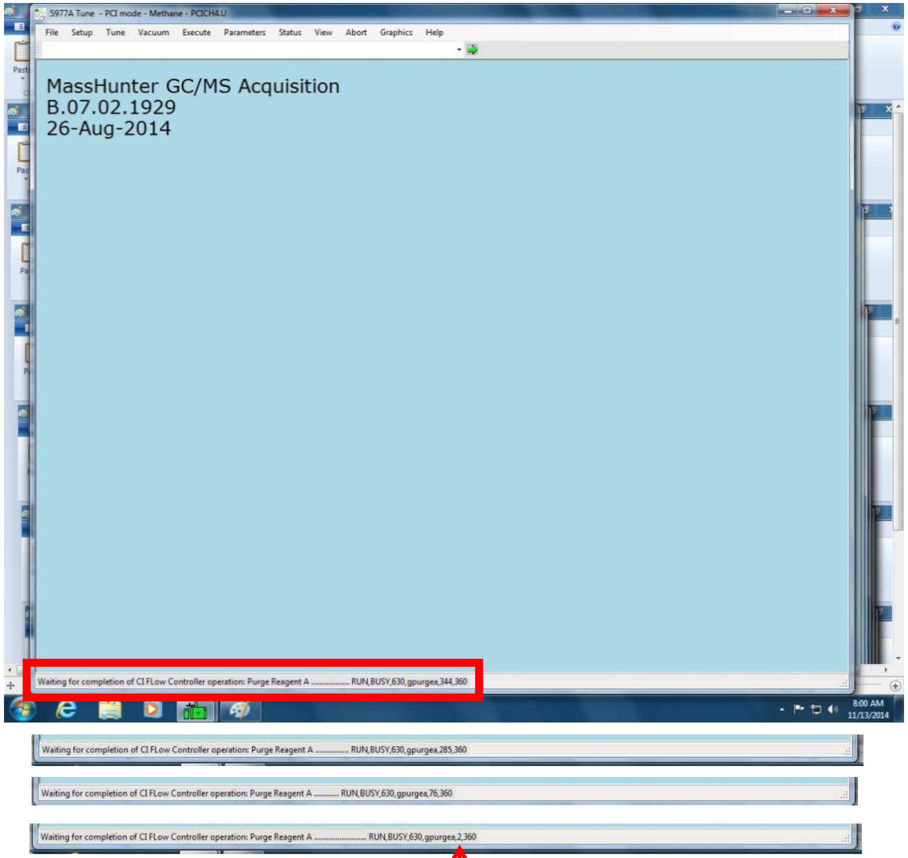


During new installation or methane tank replacement, it is necessary to purge the regulator, trap, and tubing on the CI subsystem to remove any air or moisture.

Chemical Ionization: Purge the methane gas line

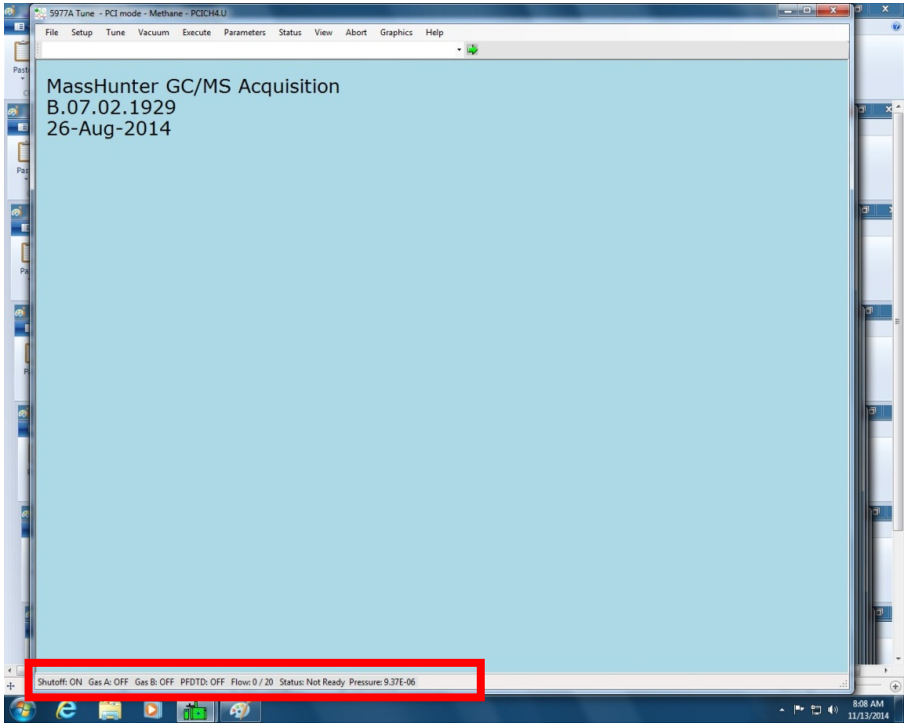


Purge the line for six minutes. This is the default and should not be overridden.

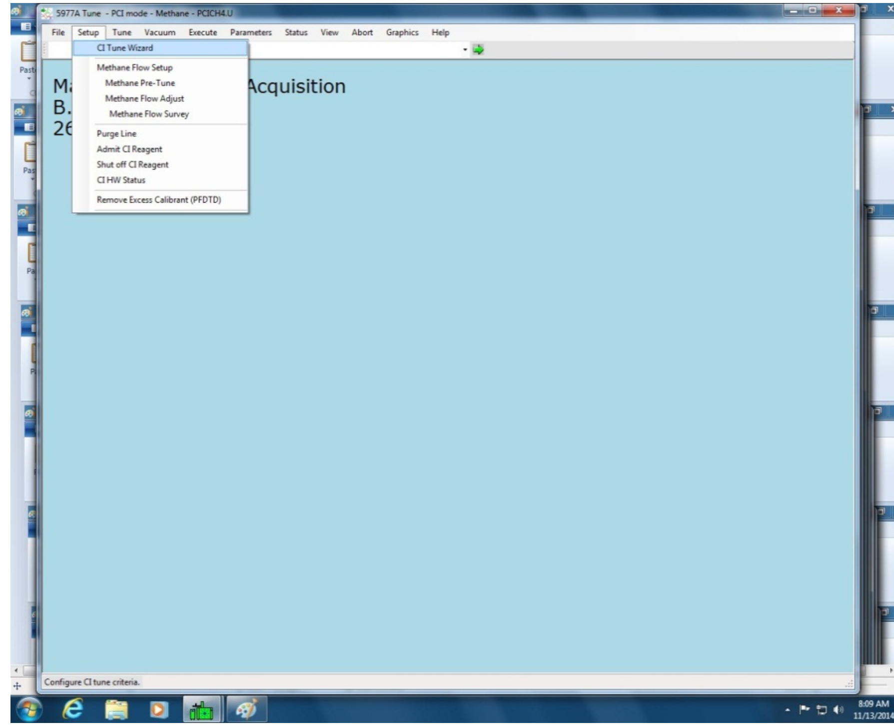


Two seconds left…

Chemical Ionization: Check the CI Tune Wizard.



This shows the status of the valves, flow and pressure.



Select CI Tune Wizard. This will step you through the settings.

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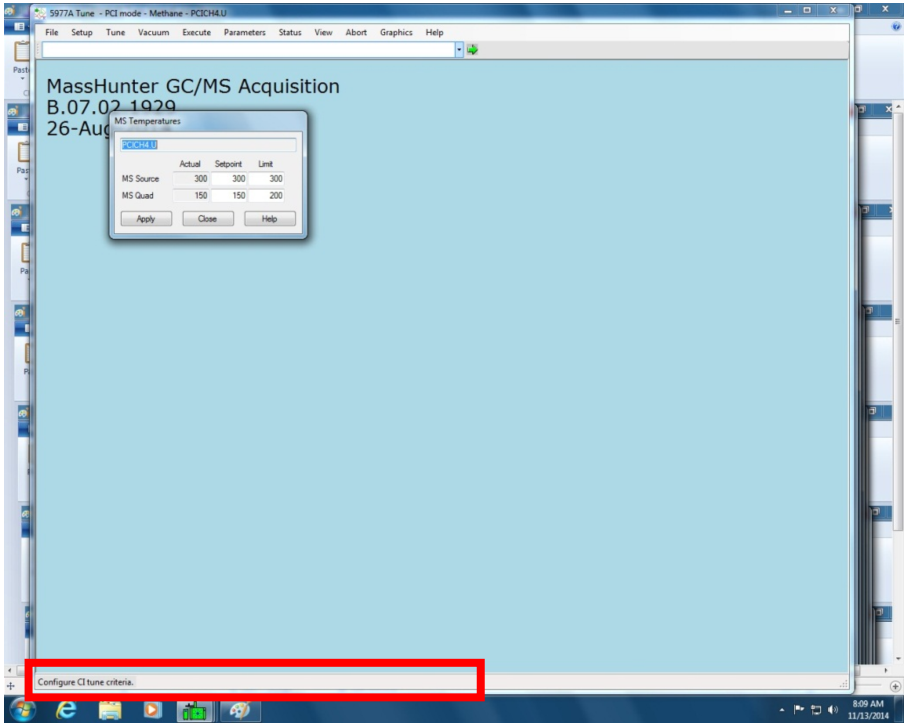
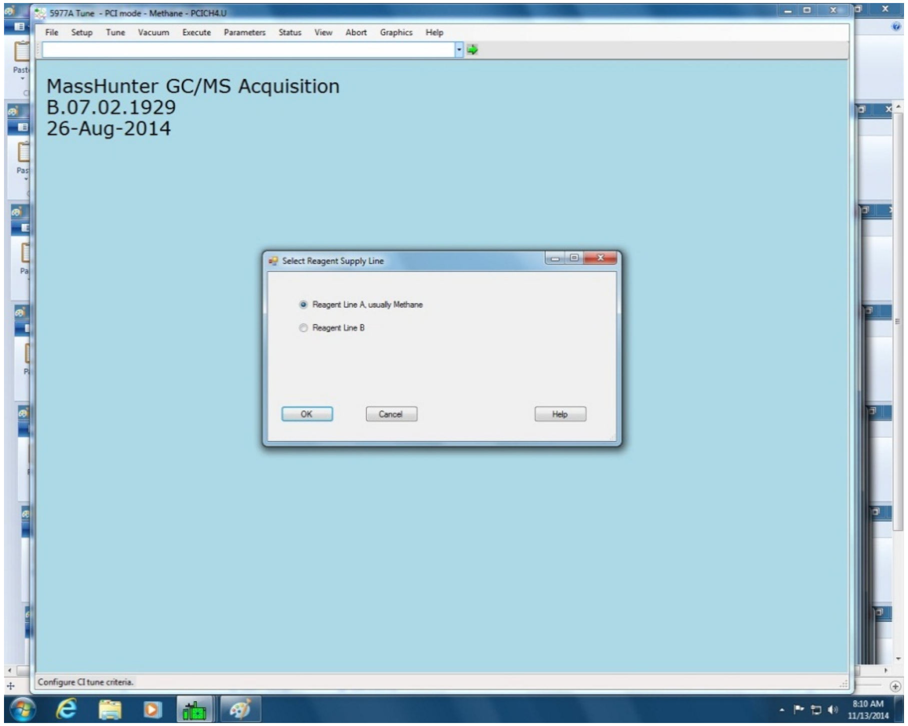
Chemical Ionization: Check the CI Tune Wizard.

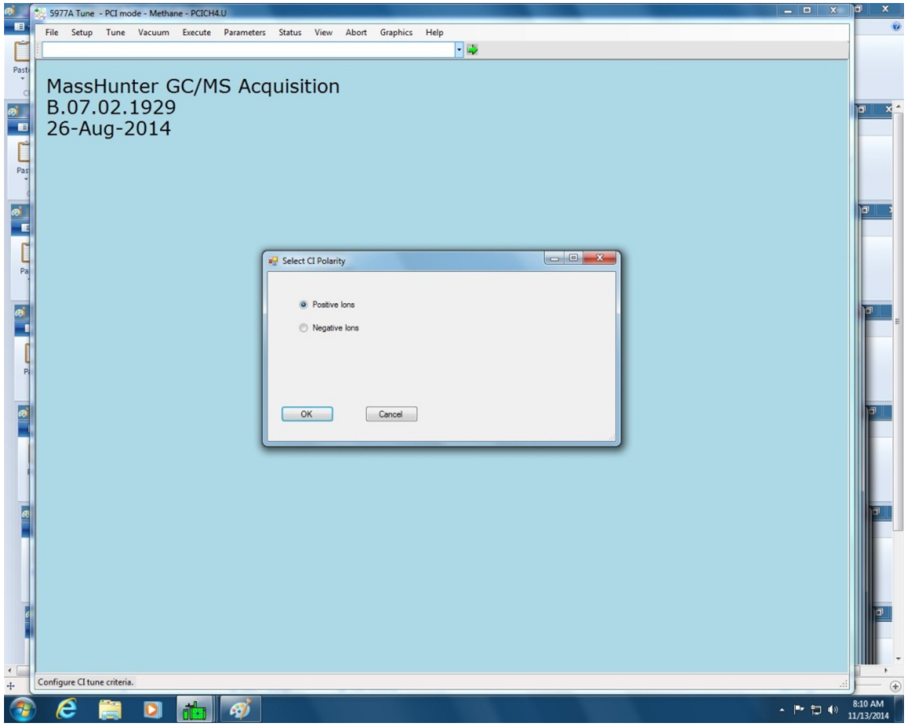


Source and Quad temps. For PCI the source MUST be at 300. Be patient and allow time for the entire source to become thermally stable. At least one hour, but preferably overnight.

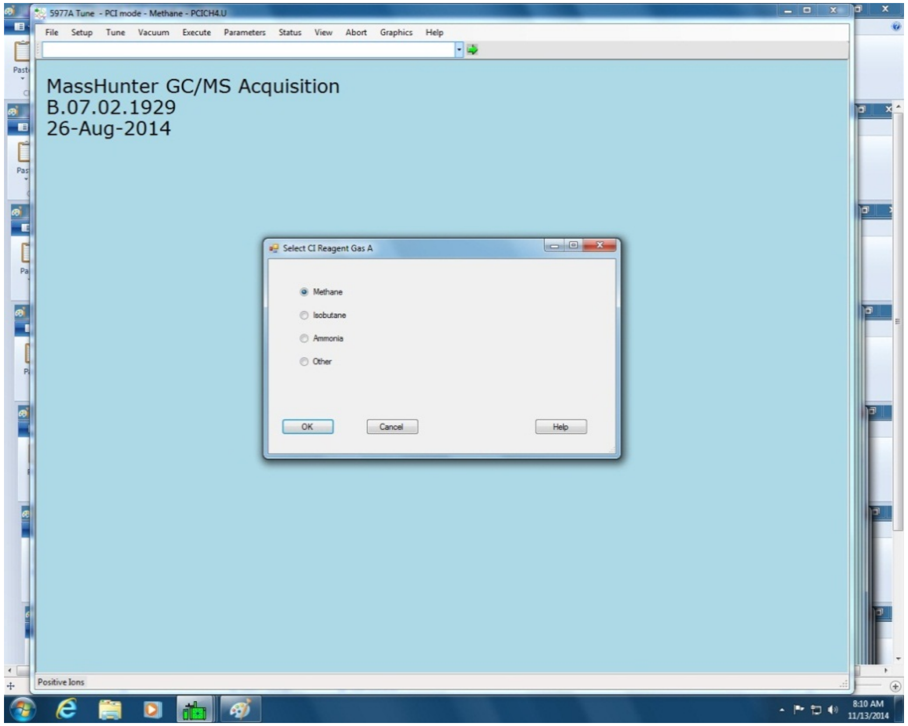


Select Reagent gas.

Chemical Ionization: Check the CI Tune Wizard.

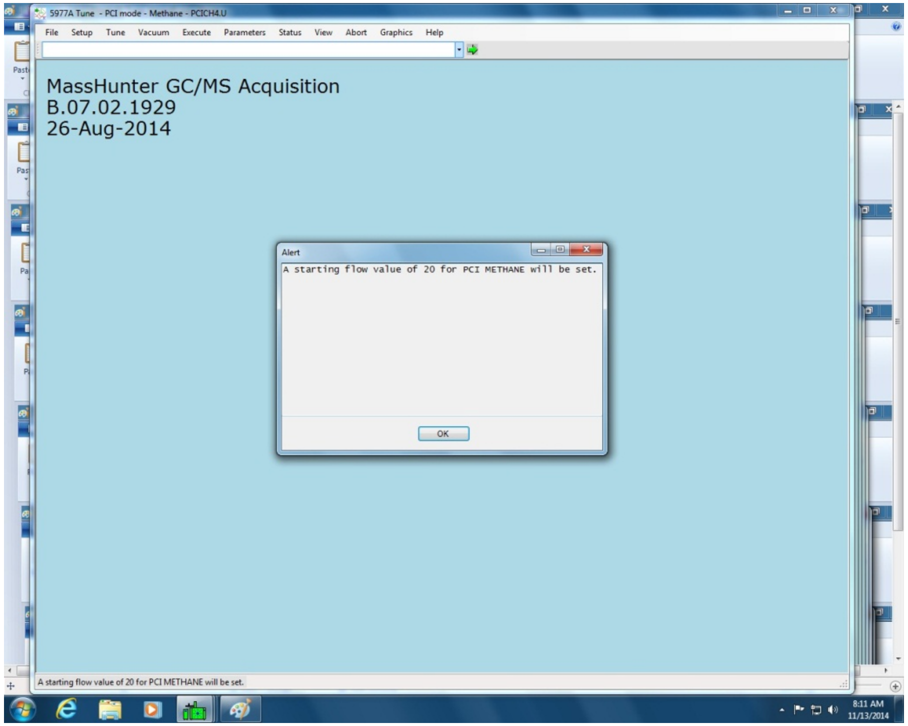


PCI or NCI.

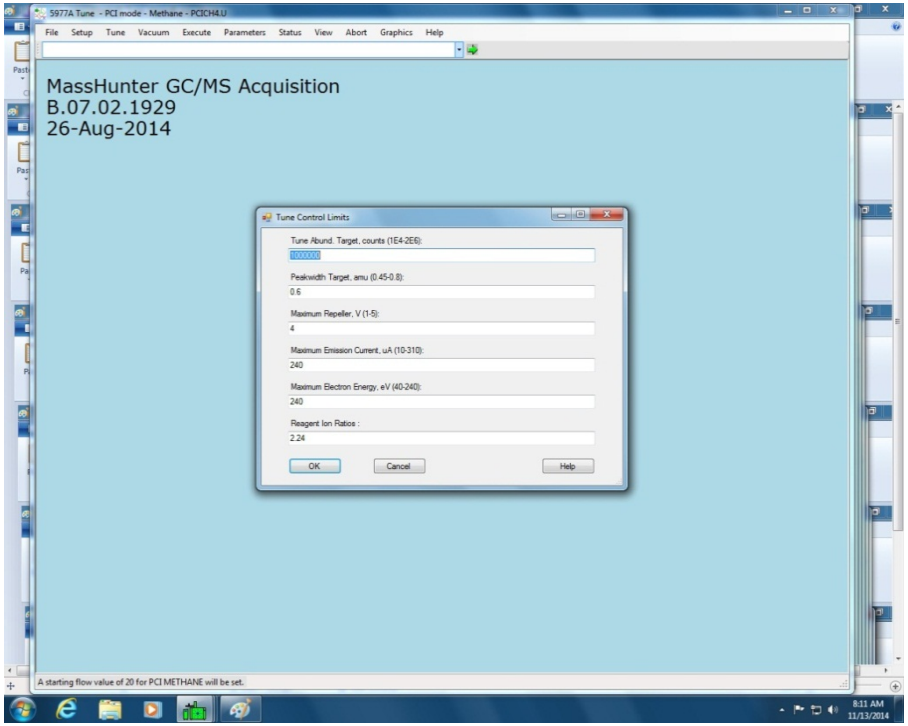


Which gas is it? PCI tune REQUIRES Methane.

Chemical Ionization: Check the CI Tune Wizard.

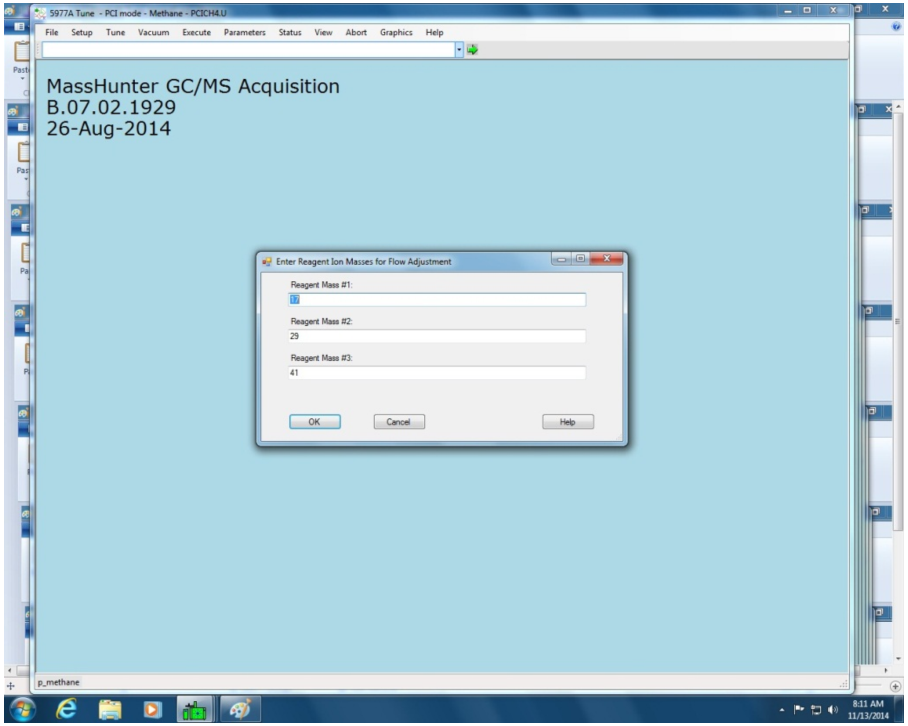


It will start with the flow at 20%.

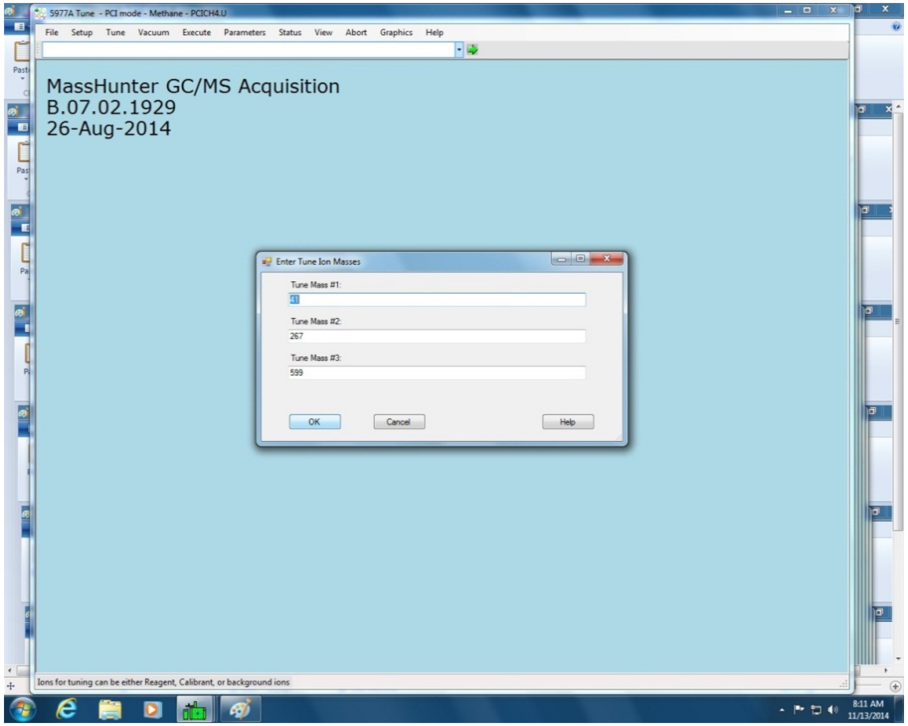


Defaults

Chemical Ionization: Check the CI Tune Wizard.



Masses for flow adjustment. Use the defaults.



PCI Tune Ions. Use the defaults.

17 = CH_5^+ 29 = $C_2H_5^+$ 41 = $C_3H_5^+$

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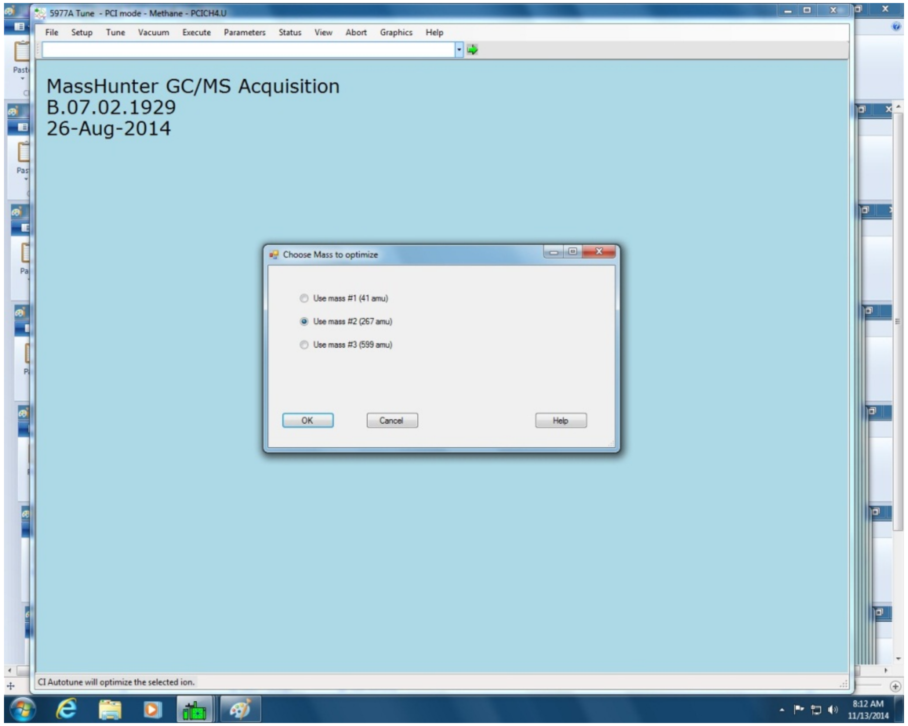
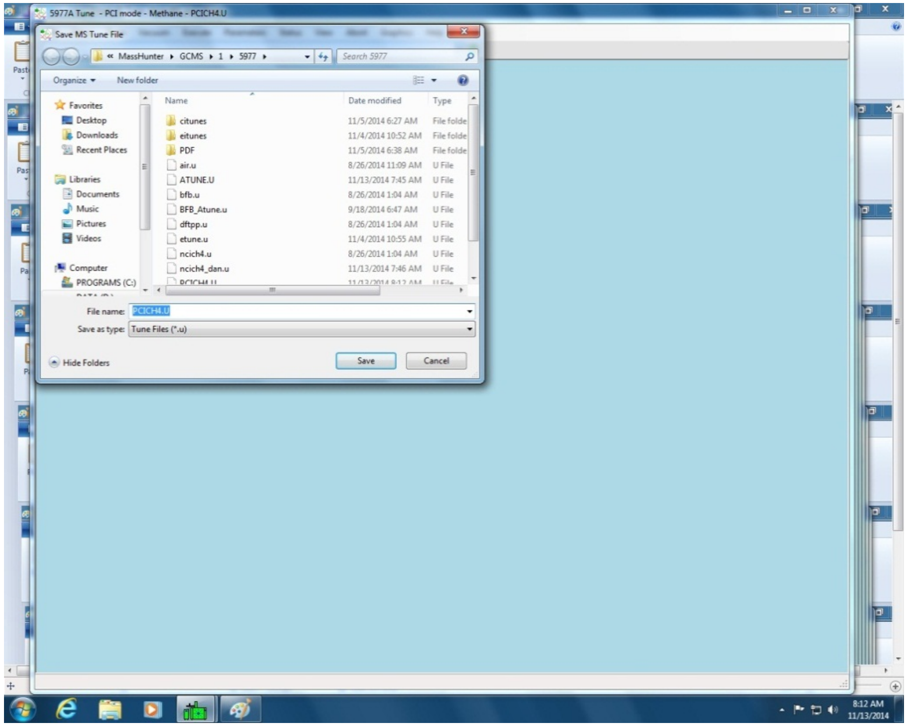
Chemical Ionization: Check the CI Tune Wizard.



Optimize the middle mass ion. This is the default.



Save the tune file. Please use the standard name or an obvious file name like PCI25Oct2018.U. Do not use any unusual characters.

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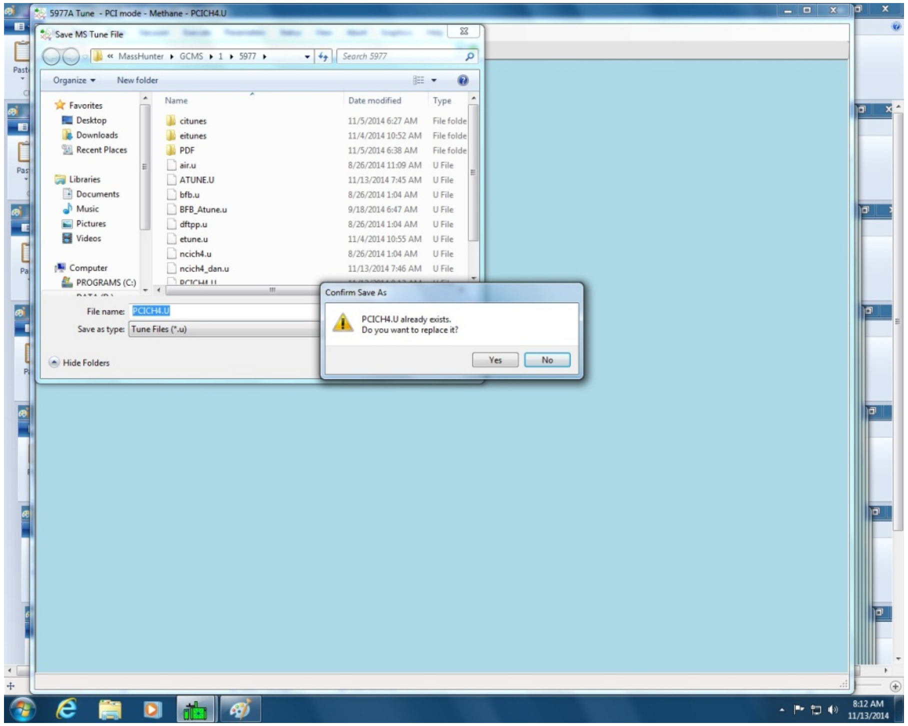
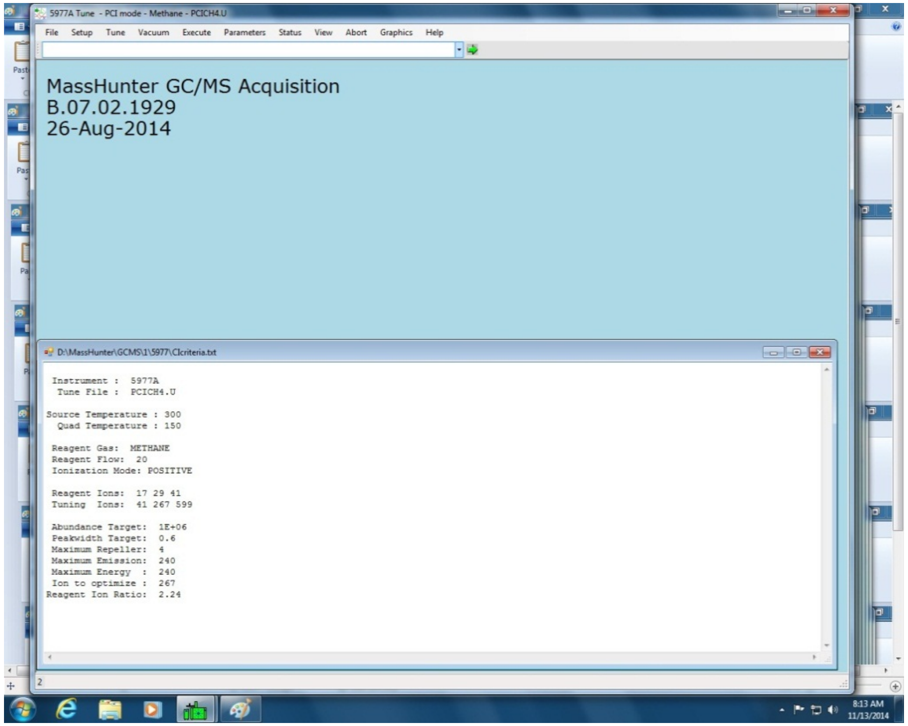
Chemical Ionization: Check the CI Tune Wizard.

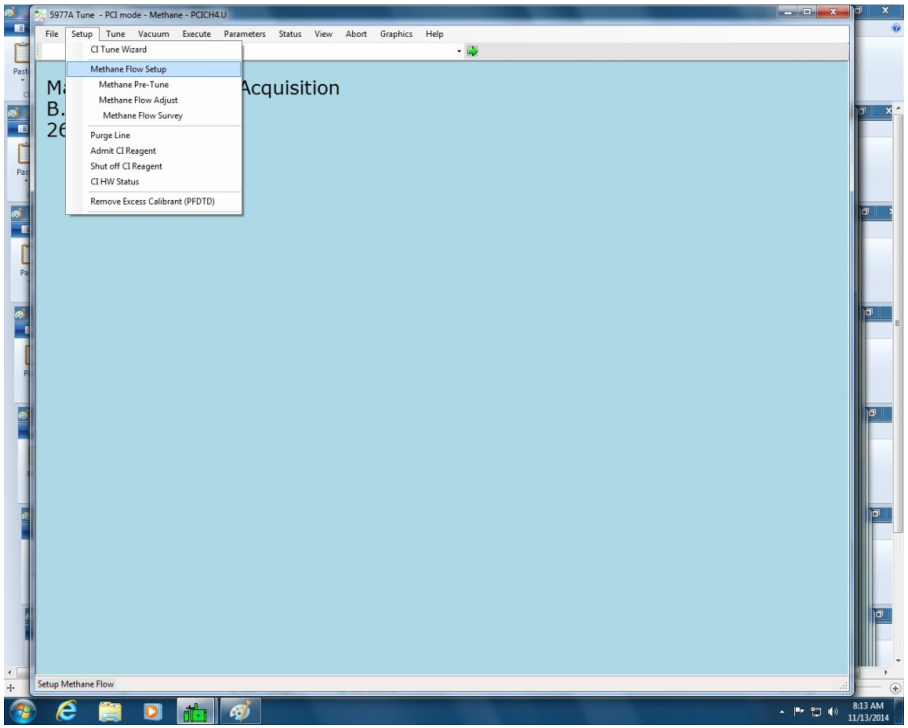


Yes, overwrite the tune file if using the default file name.

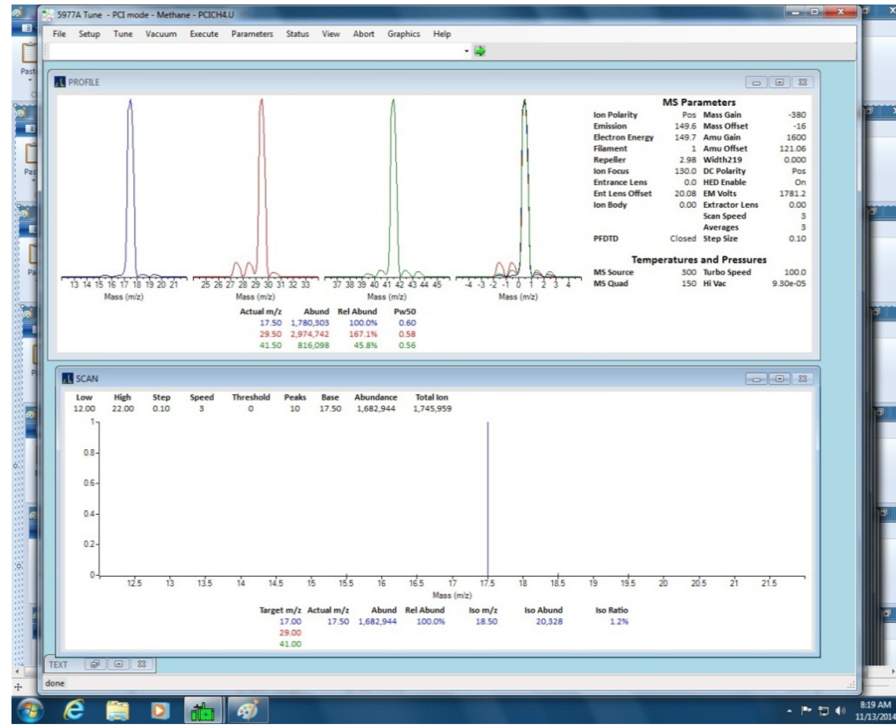


Here are the PCI criteria that will be used.

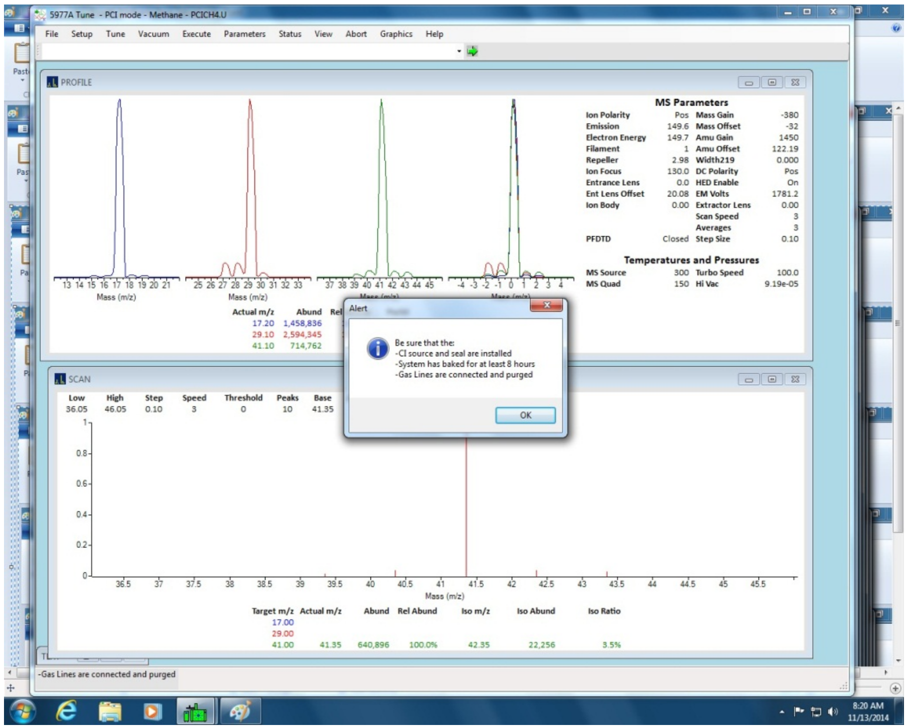
Chemical Ionization: Methane Flow Setup.



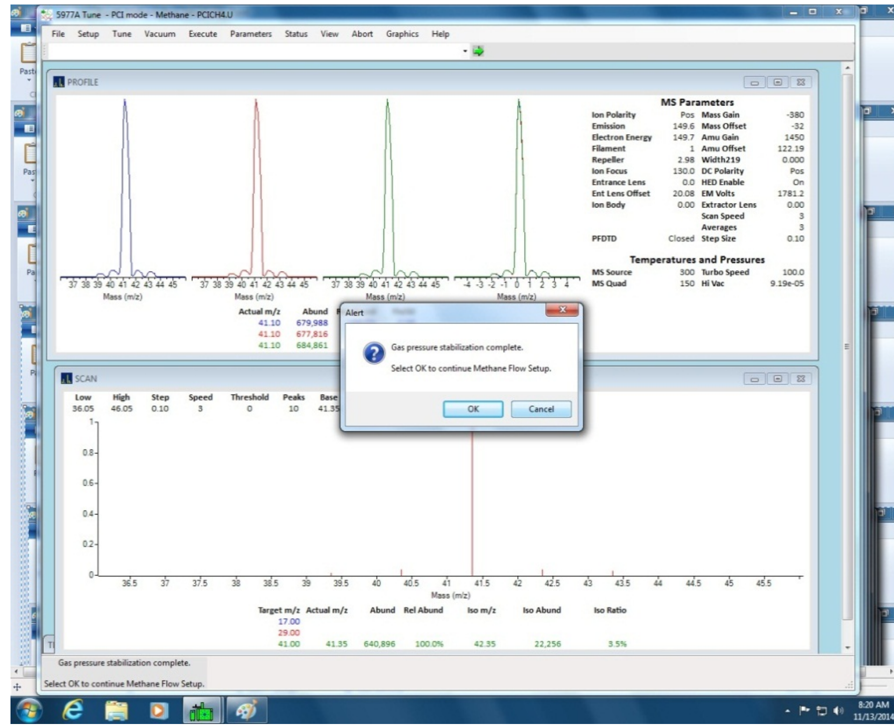
Setup, Methane Flow Setup.



Chemical Ionization: Methane Flow Setup.

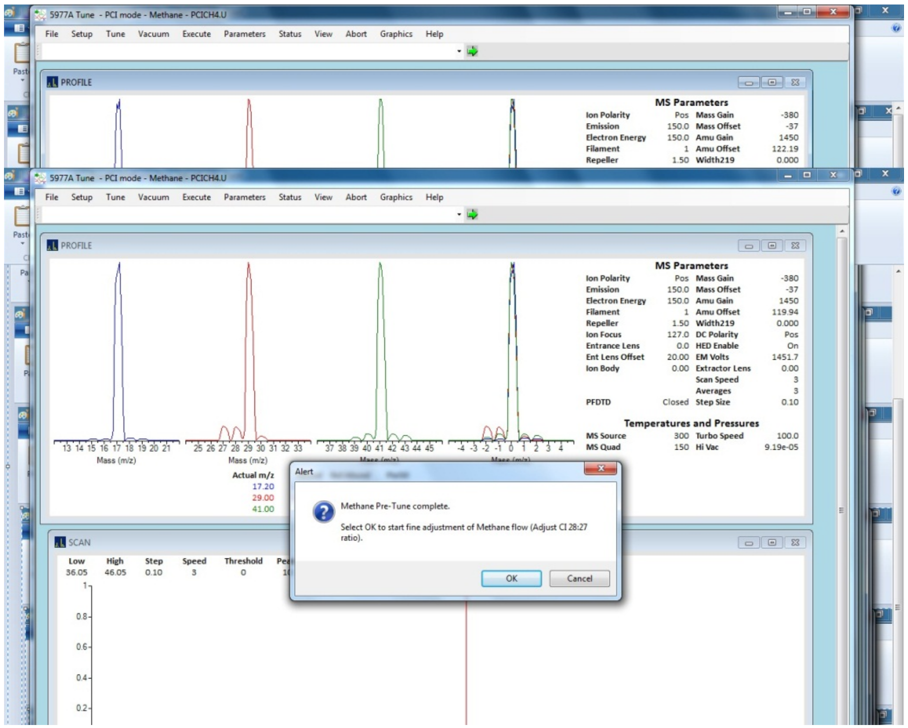


That tip seal is critical. Newer instruments have a fixed tip seal for both EI and CI applications.

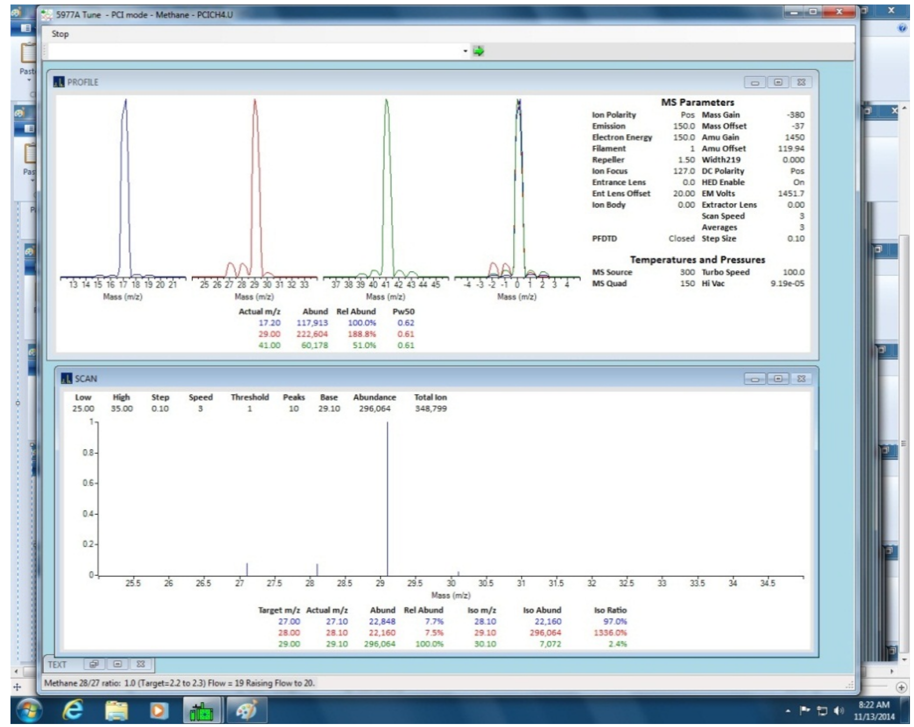


Agilent

Chemical Ionization: Methane Flow Setup.

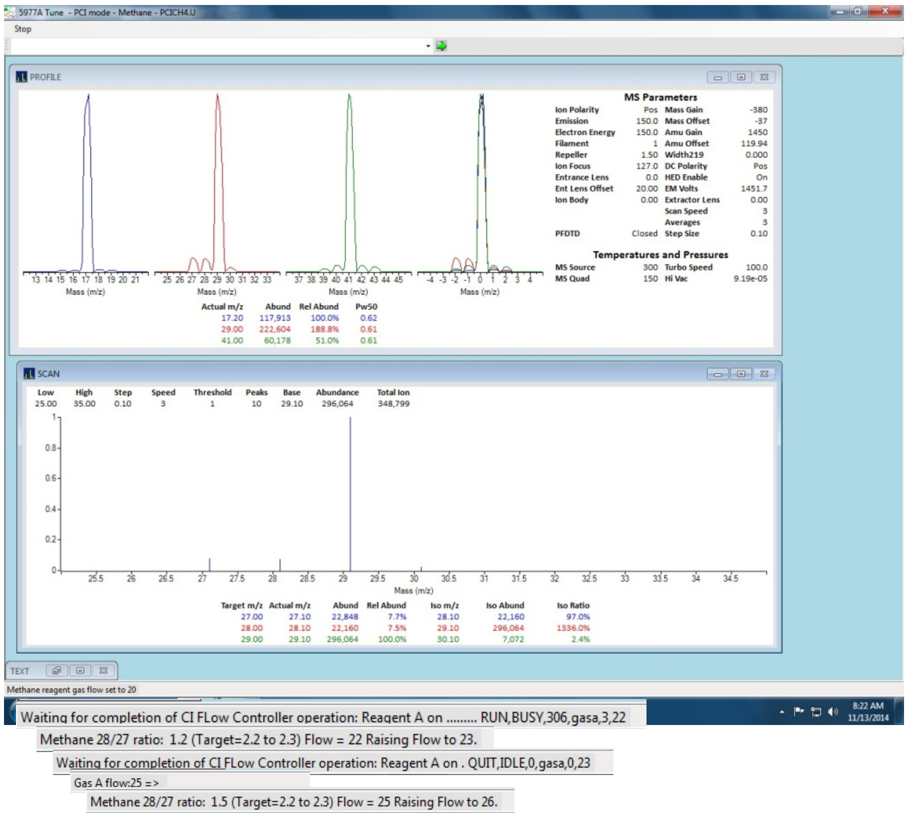


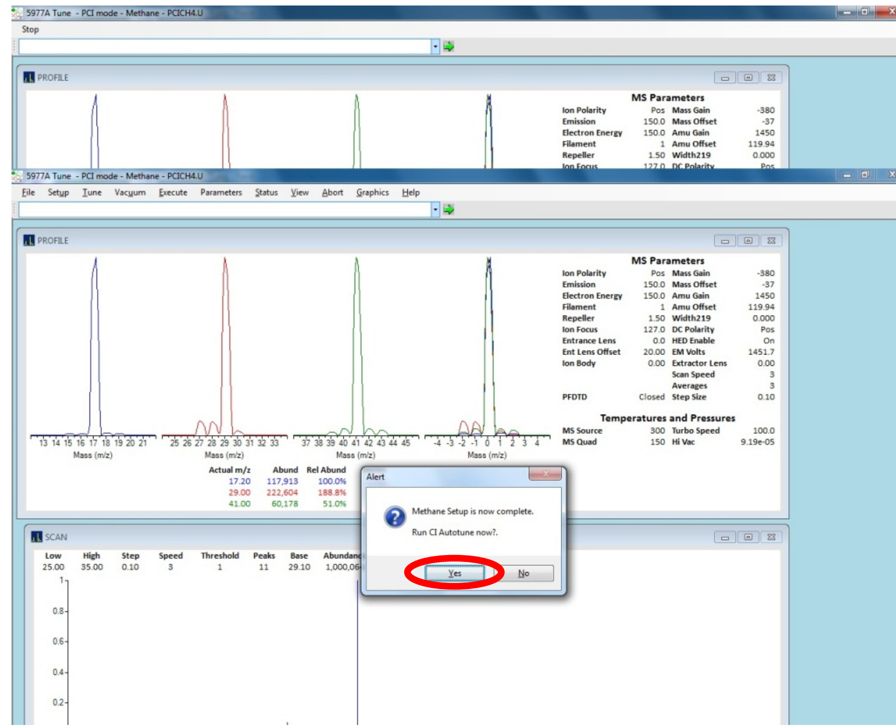
If the methane is off it will not continue from this point. It has to see some ions.



17 = CH_5^+ 29 = $C_2H_5^+$ 41 = $C_3H_5^+$

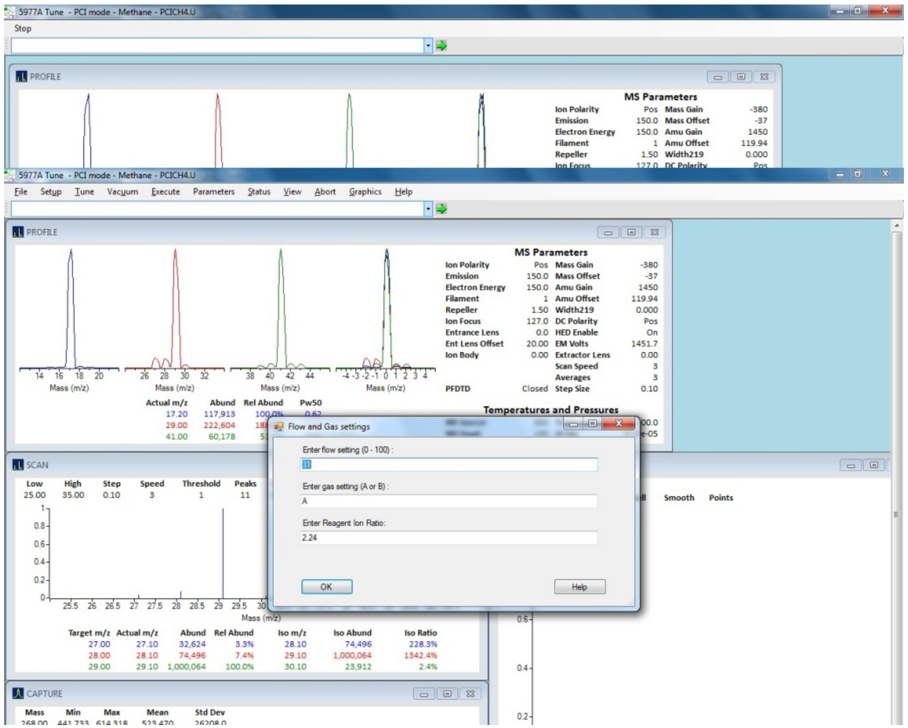
Chemical Ionization: Methane Flow Setup.



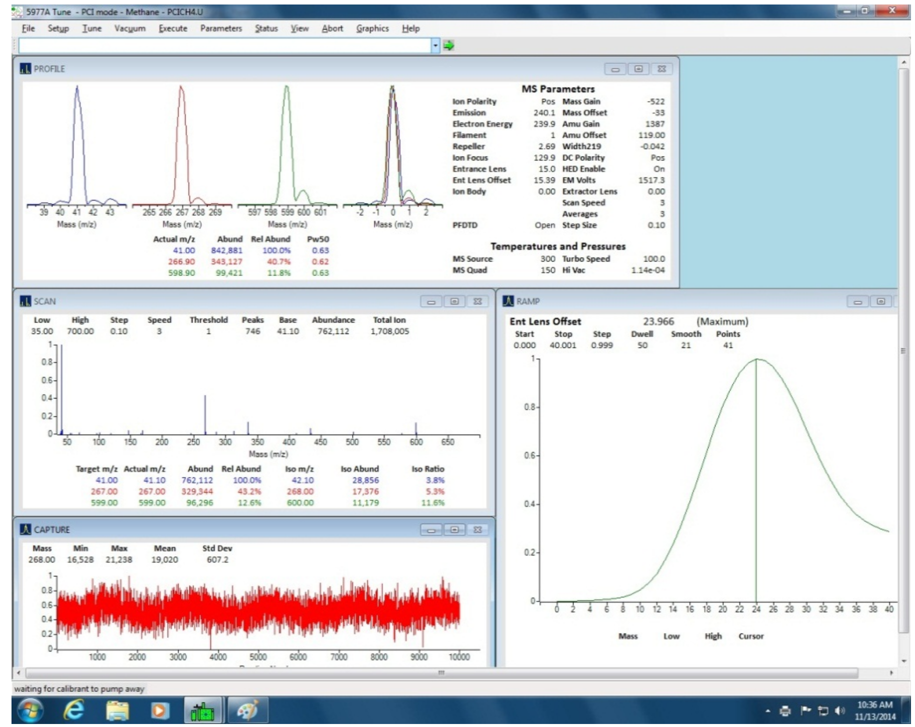


It may take some iterations…this one finished at 31%

Chemical Ionization: Autotune!

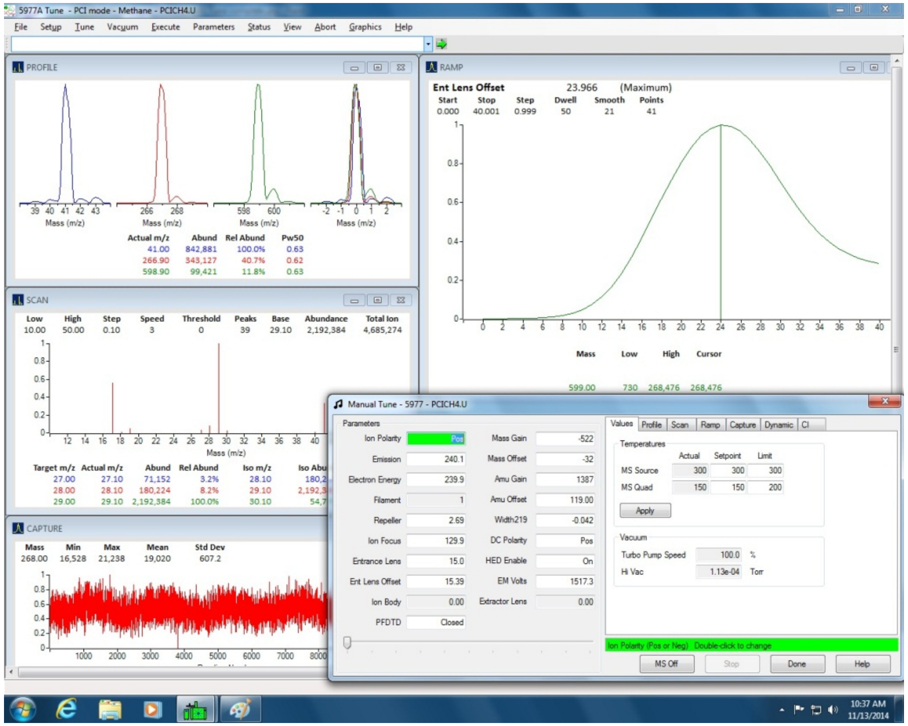


These are entered for you. Tune starts when you click on this OK button.

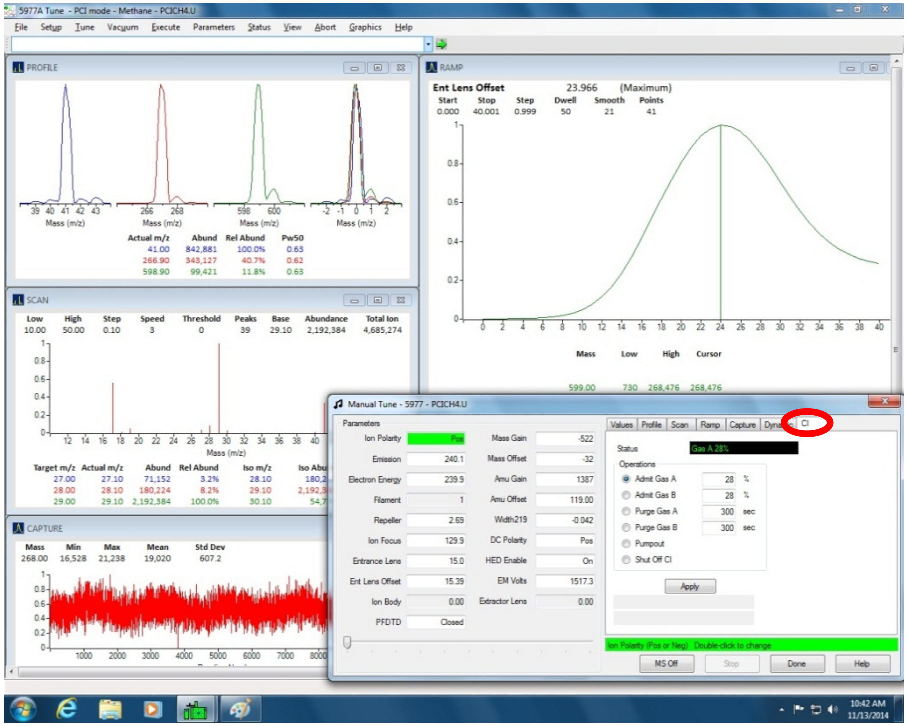


Autotune runs and the result should look something like this.

Chemical Ionization: Manual Tune.

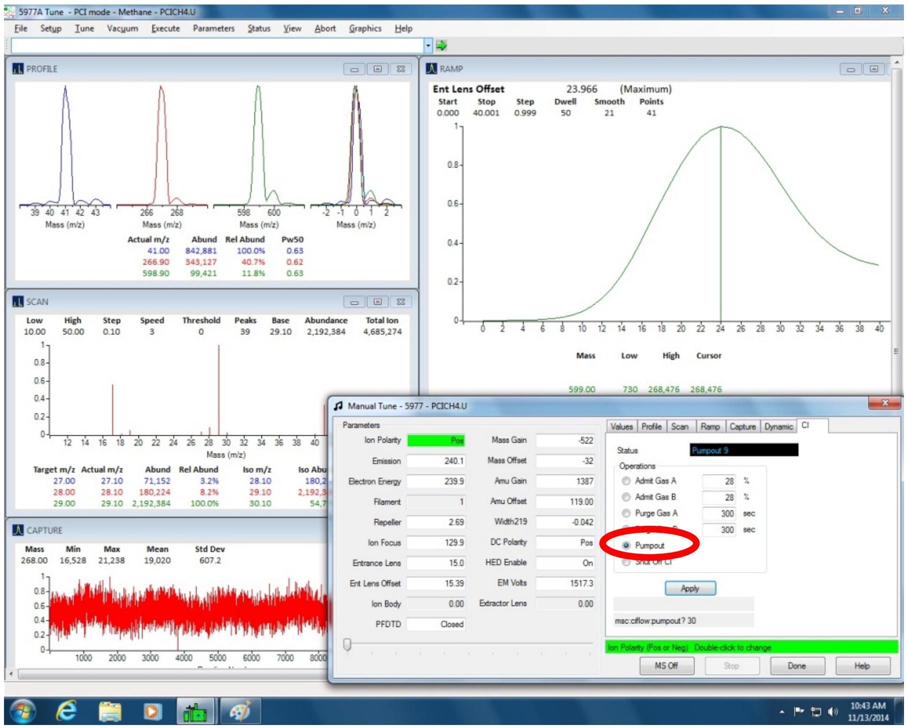


Manual Tune. Displays are leftover from autotune.

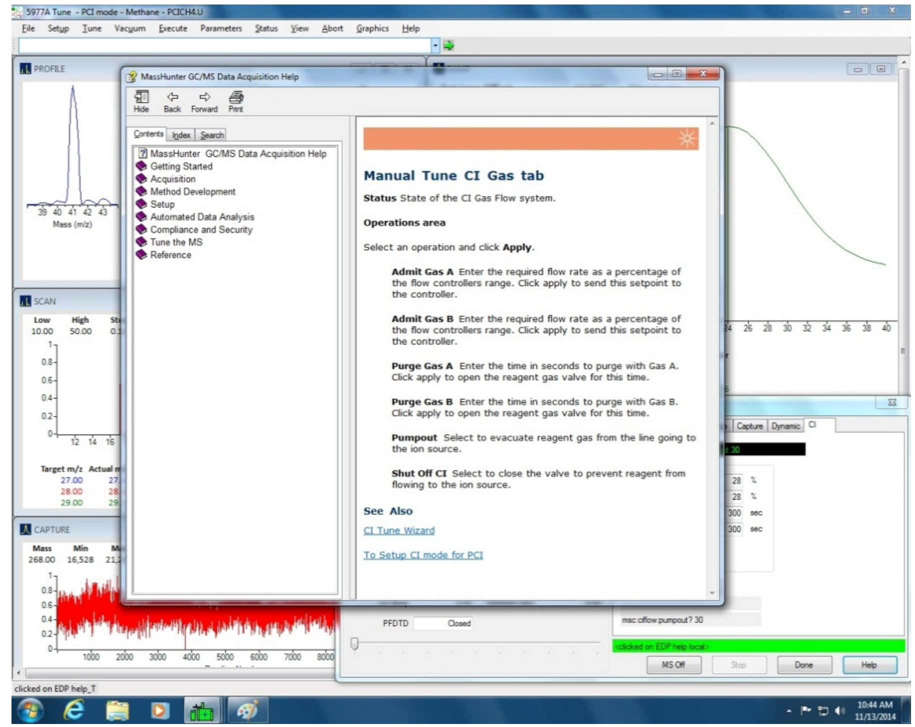


Choose the CI tab. You can control the CI subsystem here for troubleshooting.

Chemical Ionization: Manual Tune.

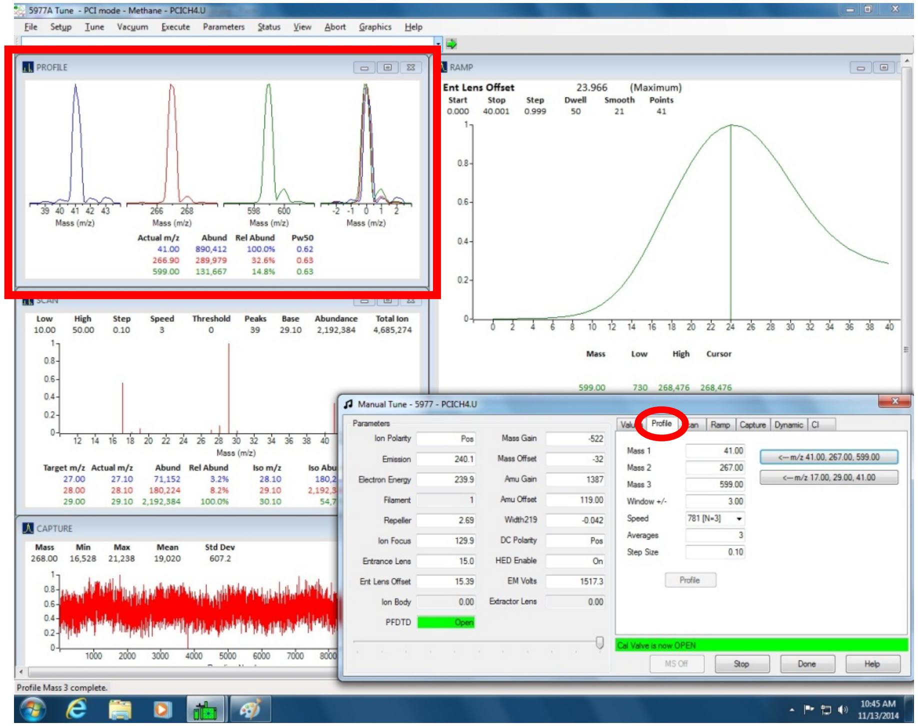


Pumpout. This closes the CI system and pumps away the reagent gas when you click the Apply button.

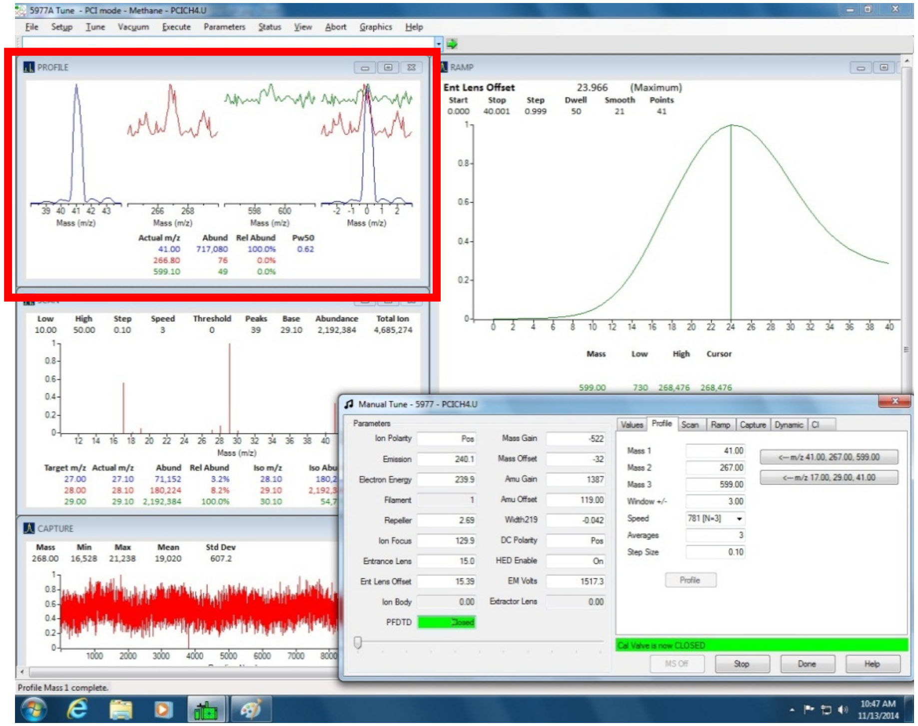


Here's the help file for this tab.   Context sensitive help is always available by pressing F1.

Chemical Ionization: Manual Tune.

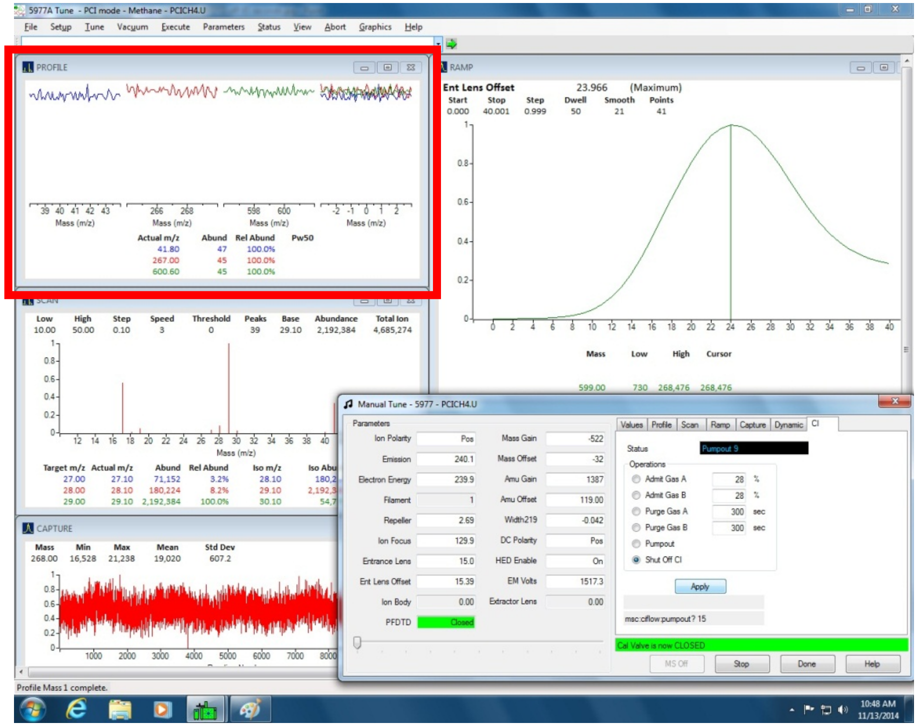


CI gas is on, PFDTD (the CI tuning compound) is Open. Start profile.

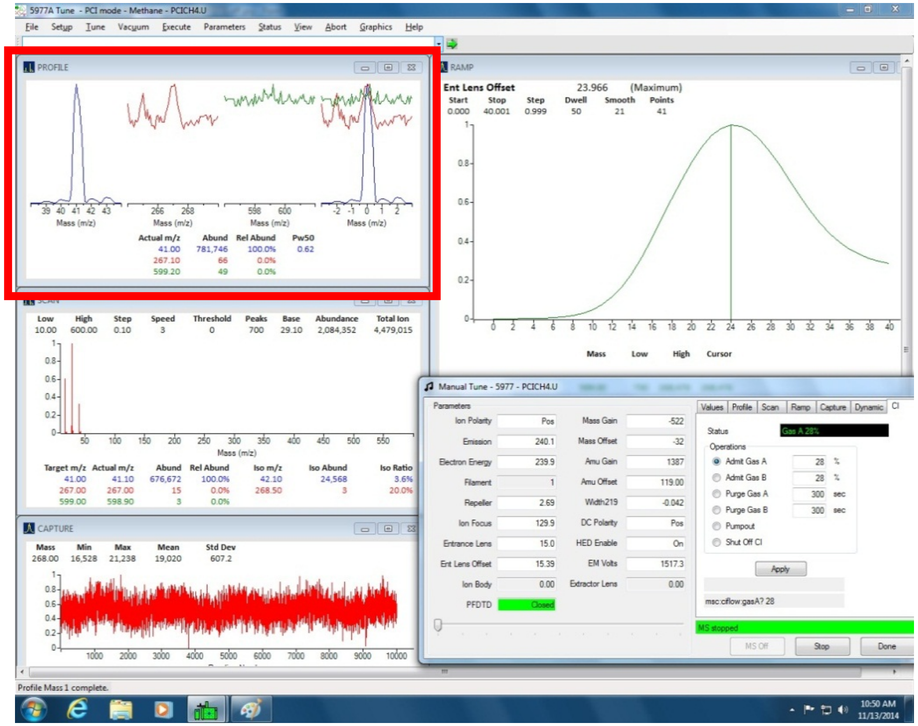


CI Gas On, PFDTD Off for ~45 seconds.

Chemical Ionization: Manual Tune.

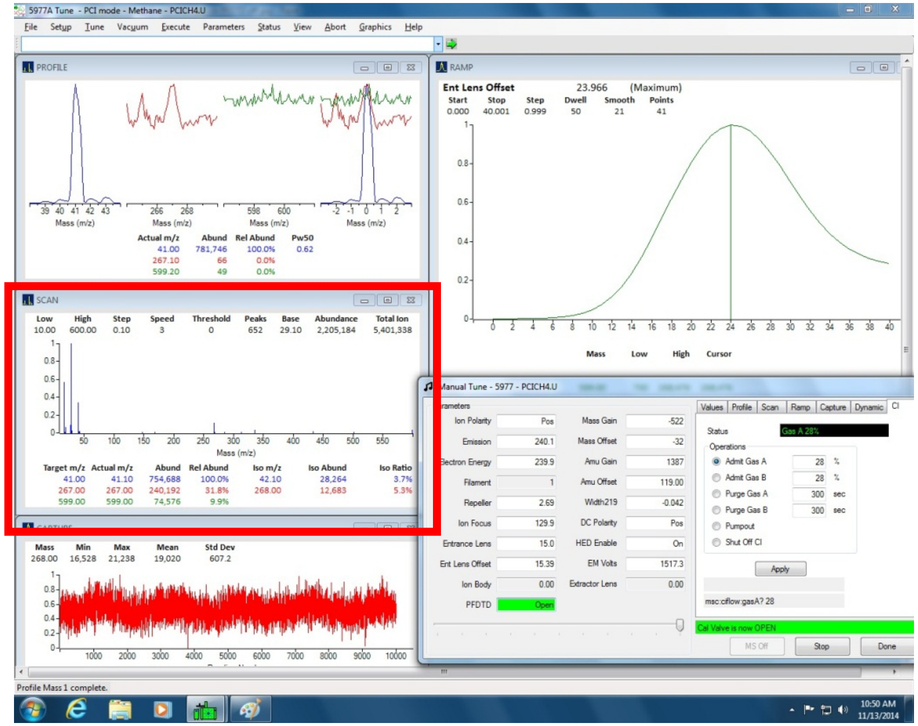


Methane Off – Shut Off CI and then Apply, PFDTD Off. No peaks in the Profile window.

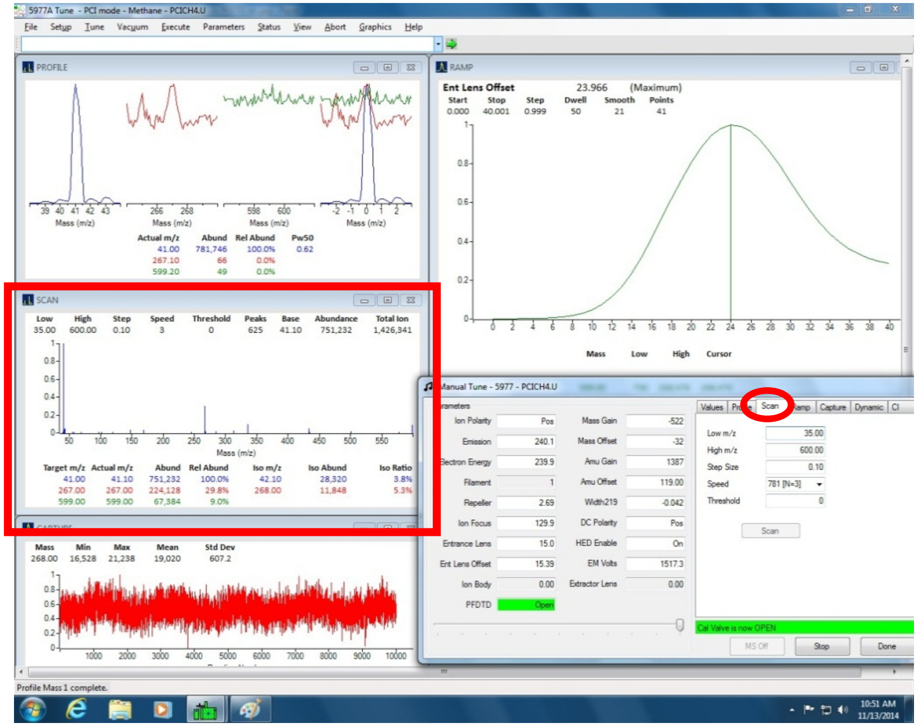


Methane On, PFDTD still Off.

Chemical Ionization: Manual Tune.

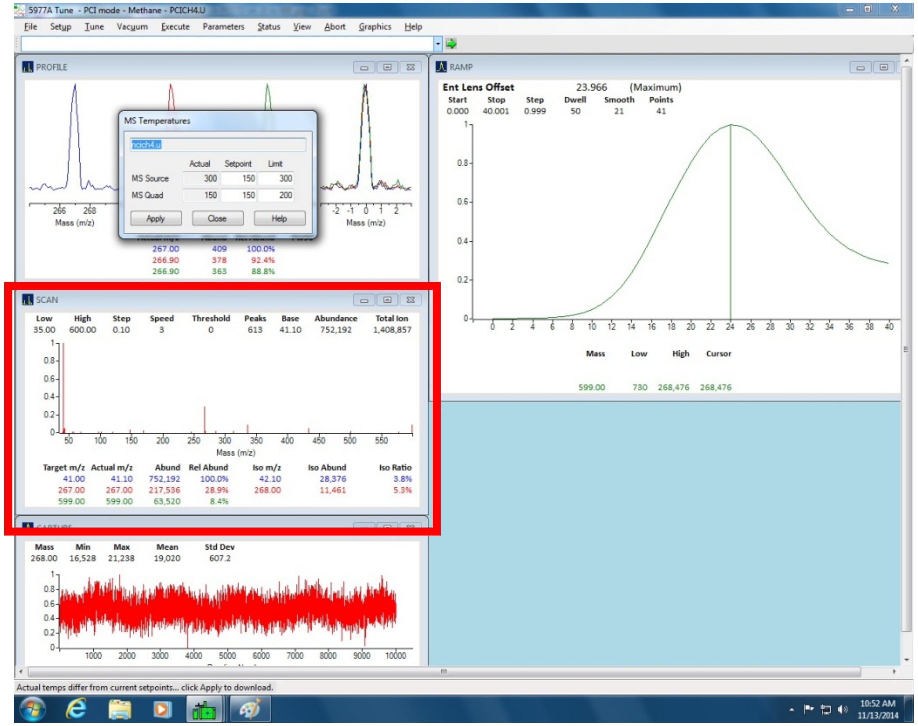


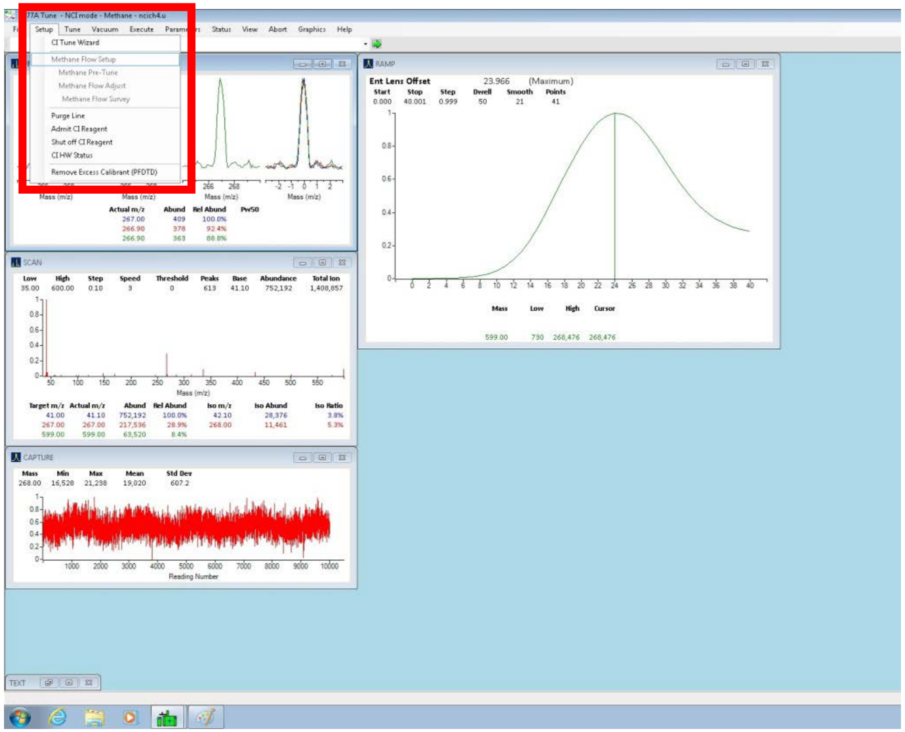
Methane On, PFDTD On. Scan range is 10-600.



Methane On, PFDTD On. Changed Scan range to 35-600.

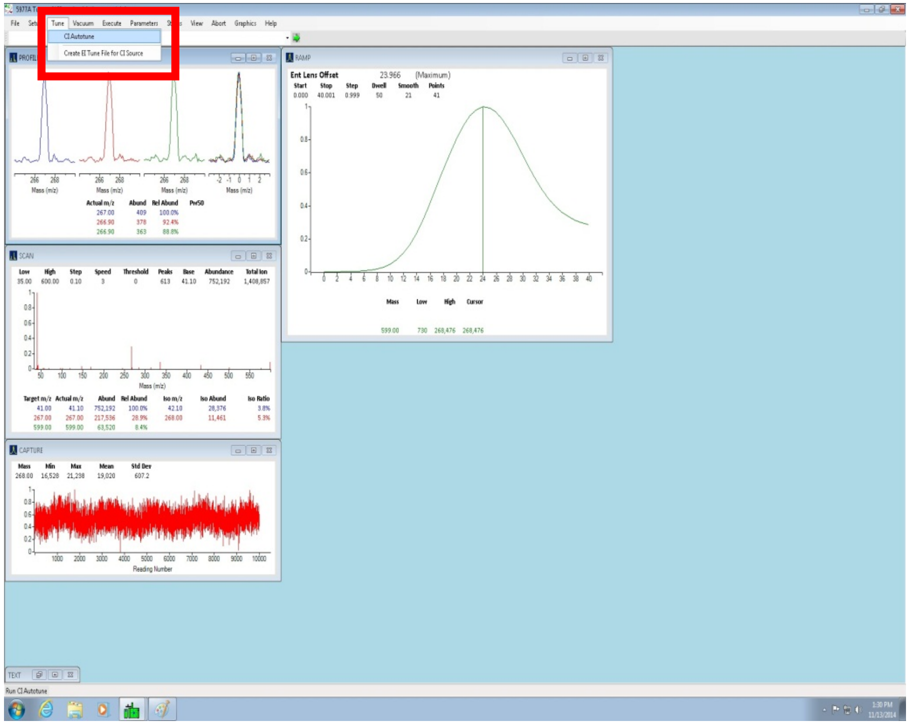
Chemical Ionization: NCI tune.



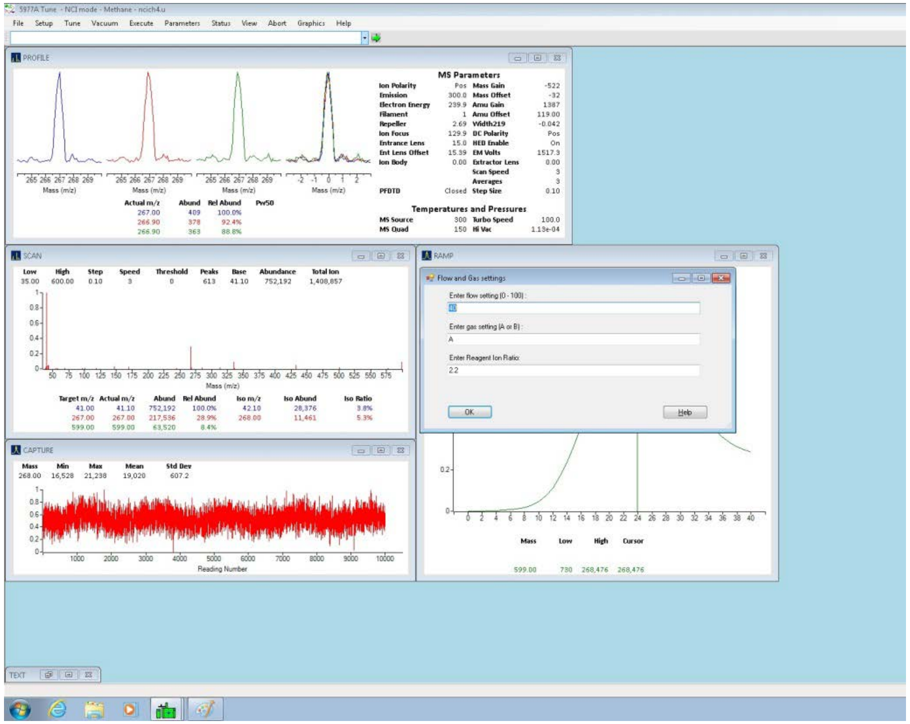


Load the NCI tune file. The source MUST be at 150 and you absolutely have to be patient and let it get cooled down and stabilized.

Chemical Ionization: NCI tune.

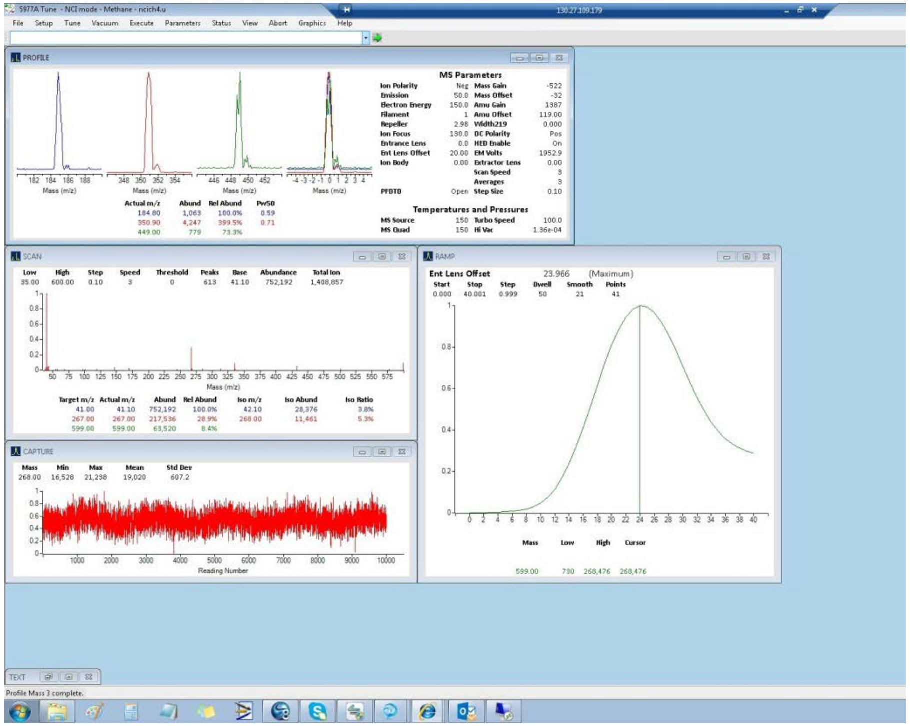


Select CI Autotune

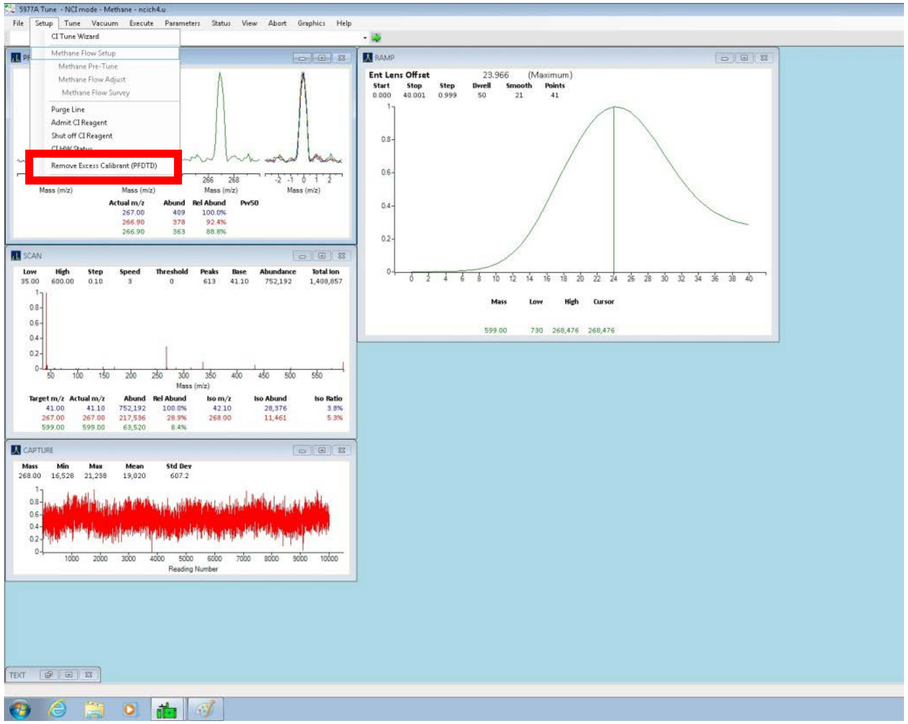


It wants a flow setting. Enter 40. That is the recommended methane gas flow for NCI.

Chemical Ionization: NCI tune.



It goes through tune. If it makes it to the end…it passes.

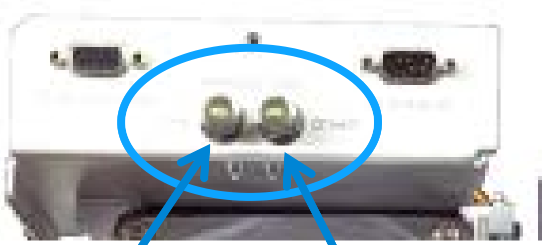


Appendices follow……….

8500-8510 PFDTD Calibrant, 1 ml ~$200 USD

Plumbing CI

Methane pressure no more than 25psi – 10psi is fine
Ammonia pressure no more than 10psi – 3 to 10 is fine

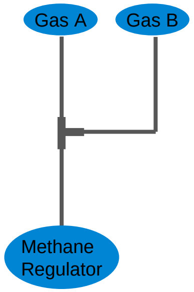


Typically for Methane

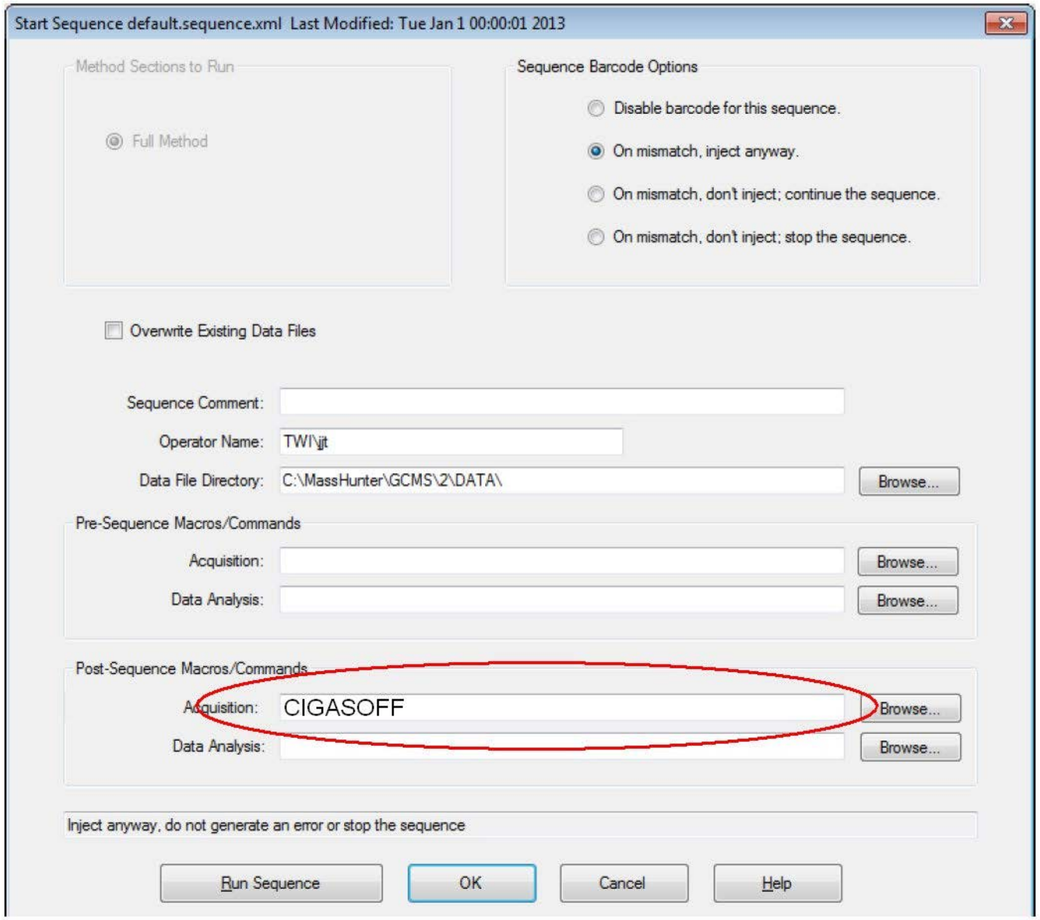
Typically for Ammonia

Stainless tubing from CI kit

Make it easier to troubleshoot in the future – install a stainless steel 1/8" swagelok tee (0100-0542 ~$71 USD) close behind the MS and plumb both connections.



Here's how to have the CI Reagent gas turn off automatically at the end of a sequence.
This has been tested in MSD Chemstation and GCMS MassHunter Acquisition.



Factory checkout and IQ/OQ of the CI system require methane.

There is a PCI autotune for methane only.

Other gases may be used and help may be provided as paid consulting.

Tips and tricks

- Helpful Troubleshooting Hints
  - EI: After tuning make sure tune abundances for m/z 69 is at least a couple 100Ks and 502:69 ratio is at least 2.4%. Run air/water check. Look at background specifically m/z 43-45, 207, 272 and PFTBA.
  - PCI: After tuning make sure tune abundances for m/z 267 is around 1M. Check background for m/z 19, 32, and 267. Check mass assignments and peak widths with same tolerances as EI. It is unlikely for PCI tune to fail. The biggest cause of failure is filament alignment and degradation and a dirty source from samples. Source cleaning is normal user maintenance. All source parts are normal customer replaceable consumables. If problems in PCI tune, switch back to EI mode and test the system. If EI works, there is nothing wrong with the non-CI MS hardware.
  - NCI: After tuning make sure tune abundances for m/z 185 is at least 100K and m/z 449 is preferably above 10K. About half of the NCI failures are due to low tune abundances and are normally caused by filament alignment, source pressure (check lens stack assembly and column nut fittings tightness), air leaks, or dirty source from samples. Source cleaning is normal user maintenance. All source parts are normal customer replaceable consumables. If NCI tune does not complete, switch back to PCI to verify that PCI still works.
  - If you are stuck without a CI filament you can use an EI filament. It is not optimum, but it will at least work.

When the instrument manuals are installed from the Agilent GC and GC/MS User Manuals and Tools DVDs the Operations Manual has a large section:: ***Operating in Chemical Ionization (CI) Mode***.

Troubleshooting:

- **Always** use the highest purity reagent gases. Methane must be at least 99.9995% pure.
- **Always** set up the MSD with methane first, even if the application uses another reagent gas.
- **Always** verify that the MSD is performing well in EI mode before switching to CI. If you struggle with CI, switch back to EI and verify instrument functionality.
- Make sure the CI ion source and GC/MSD interface tip seal are installed.
- Make sure the reagent gas plumbing has no air leaks. This is determined in PCI mode, checking for *m/z* 32 after the methane pre-tune. A peak there indicates an air leak. If such a peak is present, find and repair the leak before proceeding. Operating in the CI mode with an air leak will rapidly contaminate the ion source. (this is true for EI, too, of course)
- Make sure that the peak at *m/z* 19 (protonated water) is less than 50% of the peak at *m/z* 17.
- Check the interface tip seal by looking at the m/z 28 to 27 ratio. The normal range for 28/27: 1.5 – 5.0.
- Confirm that the MS is generating “real” ions and not just background noise. It is nearly impossible to perform any diagnostics on the system in NCI. In NCI, there are no reagent gas ions to monitor for any gas. It is difficult to diagnose an air leak and difficult to tell whether a good seal is being created between the interface and the ion volume.
- Higher mass peakwidth values give better sensitivity, lower values give better mass resolution.
- Optimum emission current maximum for NCI is very compound-specific, and must be selected empirically. Optimum emission current for pesticides, for example, may be about 200 μA.
- There is a PCI autotune for methane only, as there are no PFDTD ions produced by other gases in positive mode. That means that there is no CI autotune for other gases. PFDTD ions are visible in NCI for any reagent gas. Always tune for methane PCI first regardless of which mode or reagent gas you wish to use for your analysis
- To isolate an air leak, start by shutting the gas select valve while leaving the isolation valve and MFC open (turn on Purge and Gas Off.) If abundance of m/z 32 decreases, the problem is “upstream” of the flow module.
- Since NCI is so extremely sensitive, air leaks that are not detectable in EI or PCI can cause sensitivity problems in NCI. To check for this kind of air leak in NCI, inject OFN. The base peak should be at m/z 272. If the abundance of m/z 238 is much greater than that of m/z 272, you have an air leak.

Problems:

- Dirty Source
- Air leak
- Didn’t bake it out long enough
- Sagging or old filament
- CI gas flow incorrect
- Bad tune file

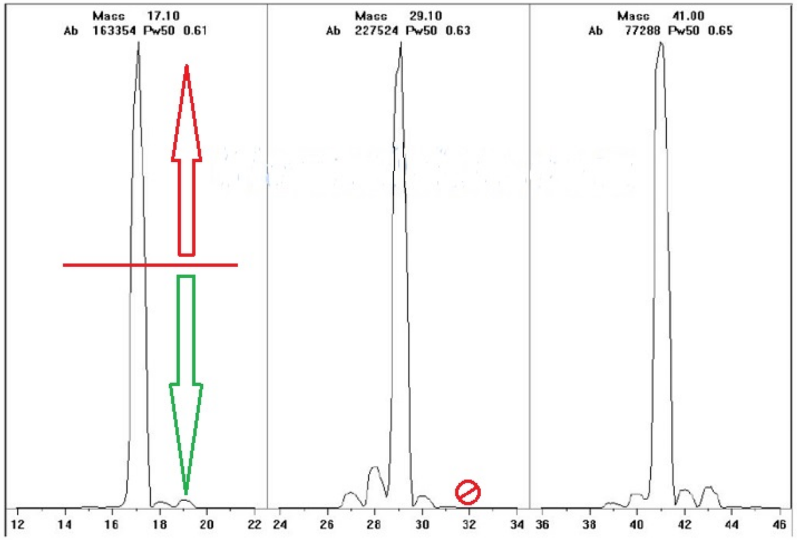
Troubleshooting:

How do I find the air leak?

1. Look for the last seal that was disturbed.
   - If you just pumped down the MSD, press on the sideplate to check for proper seal. Poor alignment between the analyzer and the GC/MSD interface seal can prevent the sideplate from sealing.
   - If you just replaced the reagent gas bottle or gas purifier, check the fittings you just opened and refastened
2. Check for tightness of seals at GC inlet and interface column nuts. Ferrules for capillary columns often loosen after several heat cycles. Do not overtighten the interface nut. Agilent fingertight nuts are highly recommended.
3. If any of the fittings ***inside*** the flow module (VCR fittings) were loosened and then retightened, the gasket must be replaced. These gaskets are good for one use only.
4. Remember that most small air leaks visible in CI mode are located in either the carrier gas or reagent gas flow paths. Leaks into the analyzer chamber are not likely to be seen in CI because of the higher pressure inside the ionization chamber.

In PCI, a peak at **32** indicates a leak.
Operating with any air will quickly contaminate the ion source and reduce filament life.

A peak at **19**, protonated water,
should not be higher than 50% of the 17 peak.



NCI Ions of interest

NCI Tune ions:

- The ones used for tuning: 185, 351, 449
- The ones not used for tuning but are still present from the PFDTD Tuning Compound: 128, 129, 166, 228, 283, 517

NCI leak related ions

- Mass 235. Rhenium oxide. This is usually a sign of a leak in the GCMS or CI flow module. (Rhenium is part of the filament's alloy)
- Mass 238 in the OFN peak. Extract this ion in Data Analysis. OFN in the presence of oxygen or water, OFN loses CF2 (mass 50) and an oxygen molecule (mass 16) gets inserted 272-50+16=238. Should be less than 5% of the OFN peak.
- Mass 254 in the OFN peak. Extract this ion in Data Analysis. OFN in the presence of oxygen or water loses CF2 (mass 50) and two oxygen molecules (mass 16 x 2) get inserted 272-50+16+16=254. Should be less than 20% of the OFN peak.

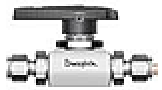
NCI related contaminant ions

- Masses 106,127,148,162, 177, and 265 are found in the detergent used to clean some of the flow module valve parts, these may be present in low levels if valve parts are not rinsed properly at the factory.
- Masses 148 and 221 (phthalates): found in rubber products such as inlet septum, gloves, and blue rubber caps on new columns.
- Masses 129, 113 and 57 come from inlet septum and result in a peak around 5 minutes.
- Masses 160 and 239 come from plastic tube used to package liners.

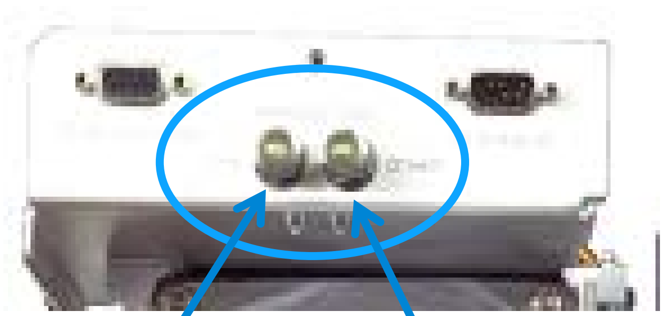
Ammonia CI plumbing

Ammonia pressure <u>no more</u> than **10** psi – ammonia may condense back to liquid if the pressure is too high.

For ammonia, the regulator must have a stainless steel diaphragm and all plumbing must be stainless steel. Purchase a stainless steel 1/8" swagelok shutoff valve (0101-1028 ~ $200 USD). It should be plumbed as close as possible to the CI flow module. That allows troubleshooting the CI subsystem without venting ammonia into the lab.



The foreline pump MUST be vented to a laboratory exhaust!



Typically for Methane

Typically for Ammonia

Stainless tubing from CI kit

Ammonia CI

Key aspects of successful operation with ammonia reagent gas:

- High purity gas (99.998% or greater)
- A connection to the CI reagent manifold that aids vaporizing of the ammonia reagent
- CI gas lines set up so no condensed droplets can make it to the MS.
- Frequent mechanical pump oil changes – at least two to four times more than the typical once per year! These additional pump oil changes are not covered by warranty or any hardware service contract.
- Ammonia may never be used with an IDP dry scroll pump.
- The MVP 070-3**C** reciprocating pump may be used with ammonia – the C is for corrosive resistance
- Use the software for automatic shutoff of ammonia following a completed sequence.
- Be safe!

Ammonia (NH_3) gas Safety.

While the Agilent GC-MS is designed for safe operation under normal usage, Ammonia gas has the following characteristics and extreme care must be taken to safely control its use.

- Flammable in the presence of open flames and sparks.
- Explosive (explosion limit 15-28 vol% in the air).
- Contact with chemicals such as mercury, halogen, silver oxide or hypochlorites can form explosive compounds.
- Irritant and corrosive

Ammonia presents a limitless number of dangers during the GC-MS operation. These include, but are not limited to:

- Combustion/explosion from leaking Ammonia.
- Health hazards from leaking Ammonia.
- Accumulation of Ammonia in the GC-MS and subsequent combustion/explosion. Ammonia can accumulate in the GC-MS in a number of unstipulated or uncommon ways. All users must be aware of the mechanisms by which Ammonia can accumulate and what precautions to take if Ammonia accumulation has occurred.

WARNING Use deliberate and careful judgment when shutting down the GC-MS. The GC-MS can also be shut down accidentally by an internal or external failure. Even though the GC-MS is shut down, Ammonia still remains in the plumbing and vacuum system. As a result, Ammonia may slowly accumulate in the vacuum pump line and possibly vent through the foreline pump. Make sure the foreline pump exhaust is properly plumbed to vent.

WARNING The following are general precautions that should be taken to prevent dangers and effects of Ammonia gas. Other precautions may be necessary depending on the setting and configuration in which you use the system. Pay careful attention to safety management when using this system.

- Store in cool, well-ventilated area with containers tightly closed.
- Make sure the Ammonia gas line is without leaks.
- Periodically check equipment for Ammonia leaks using the appropriate devices (leak detector, pressure test, etc.).
- Eliminate from your laboratory as many ignition sources as possible (open flames, devices that can spark, sources of static electricity, etc.) .
- Always turn off the Ammonia gas at its source whenever you turn off the GC-MS.
- Always turn off the Ammonia gas at its source before opening the vent valve or introducing ambient air into the GC-MS.
- Turn off the Ammonia gas at its source as soon as a power failure occurs. Do not resume operation of the GC-MS before inspecting it for damage or irregularities.
- The foreline pump exhaust vent must always be connected to a laboratory exhaust.
- The safety for external gas line and venting is the customer's responsibility.