Agilent JetClean: *In-situ* GC/MS Ion Source Cleaning and Conditioning

Application Note

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Abstract

GC/MS maintenance is a universal requirement for maintaining analytical targets during sample analysis. Rapid intra-column backflushing, one vital enhancement in the GC/MS maintenance process, has improved ion source and GC longevity, and made GC column and inlet maintenance rapid and ventless. Additionally, the elimination of late-eluting components that foul an ion source has become a salient feature of the pressure-controlled tee configurations. The frequency of ion source cleaning has been significantly lowered by these improvements, but is still required. Cooling the instrument, removing the ion source from the analyzer, mechanically cleaning the source, replacing the source, reestablishing a vacuum, and retuning and conditioning the analyzer before establishing the system sensitivity can require significant operator time. The Agilent JetClean offers the possibility of replacing the steps of cooling, removing, manually cleaning, replacing, and pumping down with an *in-situ* process that saves time and operator effort. To remove accumulated materials and restore source performance, the hydrogenic species created in the JetClean process change the conditions inside the source. This application note describes the two approaches for JetClean operation.

Agilent Technologies

Introduction

Maintenance is inevitable in the operation of a GC/MS. The GC inlet and column degrade, and require servicing (for example, replacement of the liner, septum, column cut-backs, and so forth). The frequency of this servicing is dependent upon the nature of the sample batches injected, carrier gas quality, and many other factors. The objective is to return the GC system performance to an established norm, which is usually considered the response of the target compounds in calibration standards. If, after a number of sample batches, GC maintenance alone fails to return this response, MS maintenance (source cleaning) is required. (Using the "Rapid, Universal GC/MS Backflushing" technique [1,2,3] extends the time between MS maintenance cycles, to preserve MS response, and make GC service rapid and ventless. This approach and its variants have been widely applied with great success and should be considered the norm for GC/MS configurations.)

Figure 1 shows this degradation and restoration of response by GC and MS servicing over the course of multiple batches. Note that the metric for failing may not be response alone, but loss of peak shape (chromatographic criteria), selective loss of a few sensitive target compounds, or a combination of MS signal and chromatographic criteria. Figure 1 also shows that after approximately six sample batches the response criteria dropped below an acceptable threshold. A GC service was applied (indicated by a circle), and the response returned until batch 12, then again at 18, and so on, until GC servicing at batch 24 failed to return sufficient response, indicating that MS service was required. Note that on the prior GC services, the response fails to return to the original (response ~10). This can be seen at batches 7, 13, 19, and 25, and it indicates that some losses due to the MS component continue to accumulate. Before batch 26, an MS service was done and response was almost restored. With a few injections to condition the system, the system essentially returned to its initial performance by batch 27. The trend repeats, and after three GC maintenance cycles response can only be restored by GC and MS services, as shown at batches 50, 75, and 100. This is helpful as it is predictive in budgeting time: for example, 100 sample batches will require about four MS and 17 GC service cycles for that type of sample, that preparation technique, and so forth.

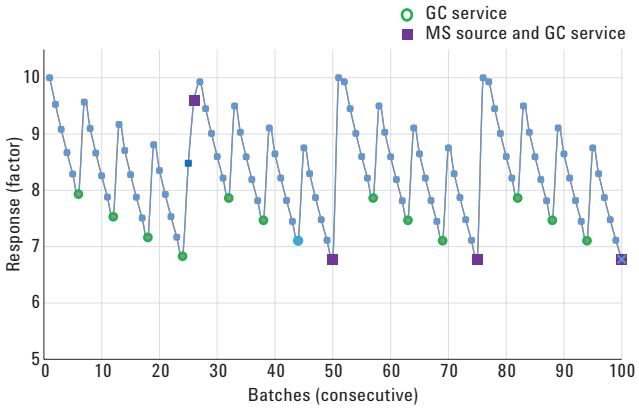


Figure 1. Response versus sample batches acquired. Every six batches, a GC service (circled) is applied to restore performance. Squares indicate that manual MS service was required.

Figure 2 shows the potential advantage of the application of an Agilent JetClean. Although GC services after batches 6, 12, 18, and so forth, are unavoidable (without improvements in sample prep, for example), an MS servicing is not required until batch 90. JetClean can be applied in two modes: concurrent with sample analysis, or as an offline, post-sequence or post-run application. These modes are referred to as Acquire & Clean or Clean Only, respectively.

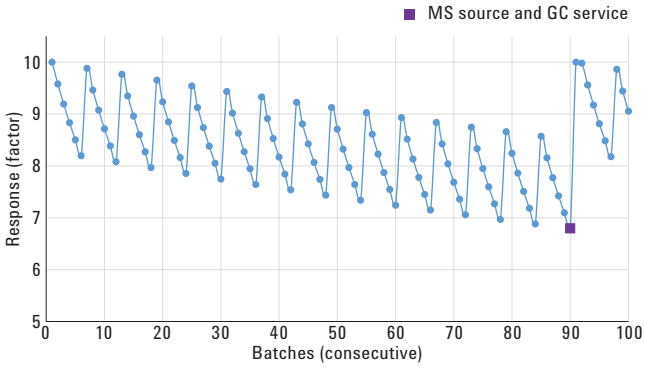


Figure 2. Response versus sample batches acquired with Agilent JetClean applied (either mode). Every six batches, a GC service (not indicated) is still applied to restore performance. But now, manual MS service is not required until after the 90th batch.

Note that Figures 1 and 2 are commonly used, but can lead to a fundamental error. This control chart approach based on response (or response factor) is used as an approximation to follow the changes expected in the compound MDL(s) or IDL(s). Figure 3 and Figure 4 show the better practice of following changes in MDL (IDL) directly.

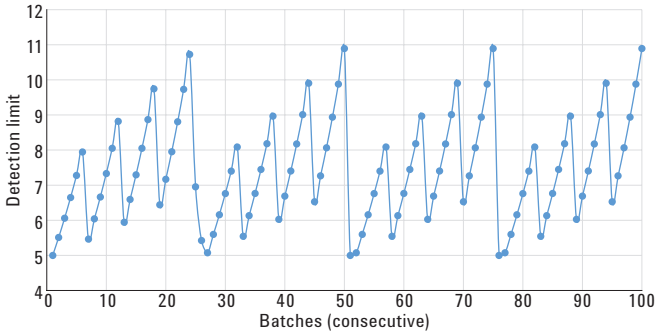


Figure 3. Detection limit versus sample batches acquired. Not indicated are GC services after batches 6,12,18, and so forth, and manual MS servicing after batches 25, 50, 75, and 100 to maintain detection limits.

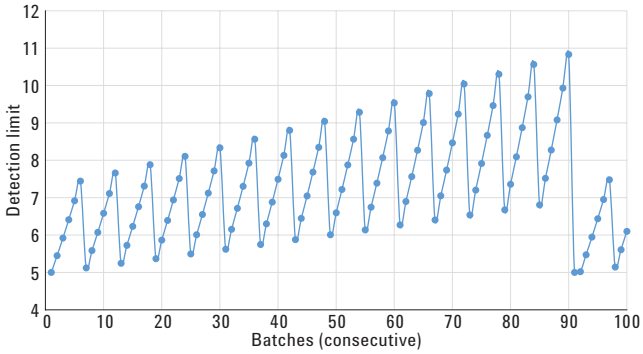


Figure 4. Detection limit versus sample batches acquired with Agilent JetClean applied (either mode). Not indicated are GC services after batches 6,12,18, and so forth, but now a manual MS servicing is not required until after batch 90.

Acquire & Clean

In the Acquire & Clean JetClean mode, the GC method (helium carrier flow, oven ramps, temperature setpoints, and so forth) are unchanged, but hydrogen is continually added directly to the ion source during sample acquisition to remove source-fouling materials. The hydrogen flow is very low ranging, from 0.13 mL/min to 0.53 mL/min in steps of 0.0665 mL/min. This is also the approach to method development. Starting with the lowest hydrogen setting, 0.13 mL/min, the MS is tuned and, using this tune file and flow setting, a standard is acquired in replicate (for example, n = 8). The spectra and peakshape are inspected for signs of degradation as some compounds may be sensitive to the presence of hydrogen species. Compound signals should not be reviewed from the viewpoint of signal height or area alone, but rather with the assistance of an IDL study. The user will find that signal RSDs, and consequently IDLs, will improve in general, and that signal drift over time will decrease. If the lowest setting is favorable, the user can try increasing the flow (by ~0.07 mL/min steps) to gain greater source longevity, although spectral aberrations such as missing ions or strongly altered ratios may eventually appear. At that point, reduce the flow and operate in that regime.

Clean Only

In the Clean Only JetClean mode, hydrogen is added and ionized in the source to reduce accumulated source fouling outside or independent of the analytical operation of the instrument. This offline action can be considered a universal way to affect a change in the source, almost equivalent to manual cleaning. Unlike manual cleaning, this can be frequently applied with great convenience, and requires less time and effort than manually removing, cleaning, and reinstalling a source. The Clean Only process can be applied as a manual step or as a method in a sequence after experience with the degree of fouling and JetClean setpoints. It is recommended that this process first be pursued manually with attention to the change in the background, and stopped when the effects diminish as will be described in the following sections.

Precautions and notes

- This application note is not a substitute for a thorough reading of the manual, which describes important aspects such as hydrogen safety, configuration, basics of the JetClean SW, and so forth.
- Observe and follow all aspects of safety as described in the manual and related documents on hydrogen use in the GC/MS. Hydrogen is a hazardous gas, and must be carefully handled and applied.
- All lines must be verified leak-free with a sensitive electronic leak detector. Soap solutions or other similar tests for gross leaks are forbidden in the GC/MS.
- All lines should be well purged to eliminate air and water. The tubing distance between the last hydrogen filter and the final connection to the Mass Flow Controller (MFC) should be as short as possible. The MFC should also be purged in the beginning and occasionally thereafter.
- The gases for EI/CI systems and timeout for shutting off hydrogen gas should be checked under the **Instrument\Gas Control Configuration** menu item. A 10-minute timeout is the default, but this MUST be modified to exceed the total cycle time between acquisitions (that is, time between filament on cycles + buffer): sum of ALS cycle duration, oven equilibrium time, oven cool down time, solvent delay time plus an additional 5 minutes for buffer.
- Prior to introducing hydrogen, the MS analyzer should show low values for air, confirming the system is leak tight.
- It is critical that an AutoTune be executed and show low air and water values prior to application of either mode of JetClean.
- When a flow of hydrogen into the source is ionized for the first time, a very high background will be observed due to adsorbed materials (mostly hydrocarbons), which will diminish over time.
- Overexposing a source to ionizing hydrogen can create source activity seen as increased compound peak tailing.

Details of setup and use

Tables 1 through 4 present useful parameters for all modes of JetClean operation. Before using any mode of JetClean, an AutoTune should be acquired showing low air and water values.

Default methods are written to disk for a JetClean-enabled GC/MS system, and should be loaded and used as starting points. The user is encouraged to explore the system by increasing all setpoints, as these defaults represent the minimum values.

Table 1. Range of Agilent 5975, Agilent 5977A, and Agilent 7000B,C JetClean parameters.

Parameter/Starting setpoint	Lower end	Upper end	Comment
Hydrogen flow: (offline) Clean Only 0.67 mL/min	0.13 mL/min	3.53 mL/min	Flow steps are in 0.0666 sccm units. The standard 3-mm drawout lens configuration should not require more than ~3.5 mL/min in any Clean Only setpoint.
Emission 10 µA	10 µA	35 µA	Emission and flow increases have the greatest effects in accelerating source cleaning. To keep times short, increment these two parameters.
Duration 1 minute (as 1.3–0.25 delay)	1.3 minutes	120 minutes	Although the upper limit is high, an advantage in JetClean is time savings, so more aggressive parameters should be explored.
Source temperature Use operating tune file setting	150 °C	350 °C	Start with your acquisition method's Tune File source temperature and quadrupole temperature to save time.
Hydrogen flow: (online) Acquire & Clean 0.13 mL/min	0.13 mL/min	0.53 mL/min	Most applications will use very low settings for (Online) JetClean Acquire & Clean (< 0.53 mL/min), and step up this parameter in small increments.

Table 2. Range of Agilent 5977B HES JetClean parameters.

Parameter/Starting setpoint	Lower end	Upper end	Comment
Hydrogen flow: (offline) Clean Only 0.67 mL/min	0.13 mL/min	3.52 mL/min	Flow steps are in 0.0666 sccm units. No setpoint should exceed ~3.5 mL/min in any Clean Only method setpoint.
Emission (µA) 10 µA	10 µA	100 µA	Recommended maximum is 50 µA; low setpoints will take some time to stabilize.
Duration 1 minute (as 1.3–0.25 delay)	1.3 minutes	120 minutes	Although the upper limit is high, an advantage in an Agilent JetClean is time savings, so more aggressive parameters should be explored.
Source temperature Use operating tune file setting	150 °C	350 °C	Start with your acquisition method's Tune File source temperature and quadrupole temperature to save time.
Hydrogen flow (online) Acquire & Clean	0.13 mL/min	0.53 mL/min	Most applications will use very low settings for (Online) Agilent JetClean Acquire & Clean (< 0.53 mL/min) and step up this parameter in small increments.

Table 3. Range of Agilent 7010 HES JetClean parameters.

Parameter/Starting setpoint	Lower end	Upper end	Comment
Hydrogen flow (offline) Clean Only 0.67 mL/min	0.13 mL/min	3.52 mL/min	Flow steps are in 0.0666 sccm units. No setpoint should exceed ~3.5 mL/min in any Clean Only method setpoint.
Emission (µA) 10 µA	10 µA	100 µA	Recommended maximum is 50 µA; low setpoints will take some time to stabilize.
Duration 1 minute	1 minute	120 minutes	Although the upper limit is high, an advantage in an Agilent JetClean is time savings, so more aggressive parameters should be explored.
Source temperature Use operating tune file setting	150 °C	350 °C	Start with your acquisition method's Tune File source temperature and quadrupole temperature to save time.
Hydrogen flow (online) Acquire & Clean	0.13 mL/min	0.53 mL/min	Most applications will use very low settings for (Online) Agilent JetClean Acquire & Clean (< 0.53 mL/min) and step up this parameter in small increments

Table 4. Agilent JetClean Clean Only scan parameters per instrument and source type.

Parameter/System and source type	Agilent 5977A	Agilent 5977B HES Agilent 7000B,C	Agilent 7010 HES
eV	70 eV	70 eV	70 eV
Gain factor*	1	0.2	0.2
Mode	Scan	Scan/MS1 Scan	MS1 Scan
Starting mass**	29	29/45	29/45
Ending mass	300	300	300
Time/samples	2^5	2^5/250 msec (5)	250 msec (5)
Threshold	25	25	25

* The gain factor should be adjusted based on the parameters to keep total counts < 10^5 for any one ion current (an EM Saver should be on). As the current and H_2 flow are increased, ion counts will increase.

** Starting the mass at 29 will show the presence of N_2H^+, and indicate that the H_2 is on, and the process is operating. After that, the lower mass should be raised to encompass the range of interest, perhaps 50 and above, but here the lower edge of 45 (above CO_2) is cited.

Acquire & Clean mode

In this approach, the GC method parameters developed for sample acquisition are not altered in any way, except for the addition of hydrogen at a very low flow. This low flow is selected and set in the MS parameters, and the method is saved. Figure 5 shows the JetClean parameter method panel for concurrent acquisition operation with hydrogen. Hydrogen flow is the only parameter that is set. Tables 1 through 3 show the range in these settings for the sources supported. The hydrogen flow in the JetClean parameter method panel must match the flow used during the tuning of the instrument. For the single quadrupole (SQ), Tune MSD must be used, not Atune. The tune file is made by tuning with the selected flow first, then loading the appropriate tune file, and flow setpoint in the panel. To easily select the proper tune file, include the hydrogen flow setting (for example, Atune-H2-0_13sccm...) in the tune file name, then select and save this before the tuning is started. Warnings will be given if the tune file flow does not match the method flow setpoint. Tune reports cite the hydrogen flow setting.

Figure 6 shows the tuning panel for a JetClean-enabled GC/MS. Purge the MFC prior to tuning. The hydrogen flow setting entered is the flow setting that will be used during acquisition, and must match the parameter in the method. As the hydrogen flow increases, the response for the calibrant will decrease. In a triple quadrupole (TQ), this is readily observed because the TQ tunes at constant detector gain, whereas the SQ tunes to a target abundance, therefore, escalating gain or EMV are seen in an SQ to produce nominally the same abundance. This can be rationalized by the higher pressure in the source, the larger cross-section of hydrogen, and so forth. The relative ratios for the PFTBA target ions used for tuning in both SQ and TQ should remain approximately unchanged with the low flows of hydrogen used for the Acquire & Clean mode.

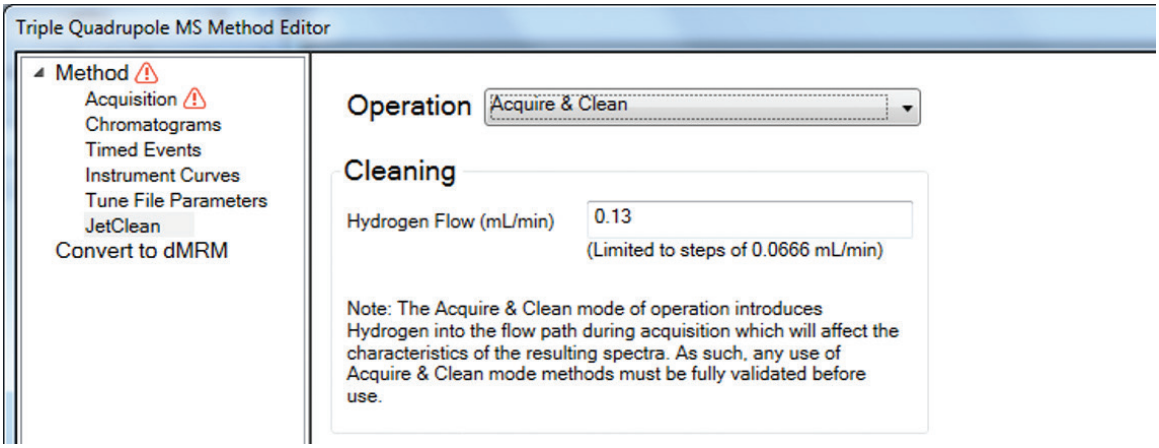
Note that in tuning with hydrogen on, there may be many low-intensity hydrocarbon-like fragments seen, so the total number of peaks in the tune report may increase. This is normal, and will increase after venting, and decrease slowly over time, eventually showing small differences in the total peaks reported. Air and water may be slightly inflated, but very high levels of water or air should result in leak checking, and perhaps purging of the hydrogen lines. (In tight analyzers, water and nitrogen will drop a bit due to production of other species, as described below.) This baseline noise will be visible during acquisition in scan mode, so the threshold setting should be raised (perhaps 2x to 3x).

The process for developing an Acquire & Clean method is to start a working GC/MS method for the analysis, then apply the lowest possible hydrogen flow setting, and re-acquire a standard in replicate. The standard data should be checked for suitable spectral characteristics such as ion ratios, background interferences, and so forth. These may be different from those observed in the absence of hydrogen. If no detrimental effects are observed, there are two choices:

- Operate with this flow setting, acquire standards and samples, create calibration, and so forth.
- Increment the hydrogen flow, retune, and save the tune file with this new flow setting, and again acquire a standard replicate and examine it.

Before using the method, appropriately revise gain factors, thresholds, and so forth. Some compounds are more immune to the presence of hydrogen than others. The greater the polarity of the compounds due to the presence of polar groups containing oxygen nitrogen and sulfur or phosphorus, the more likely effects may be present. Compounds that are less fragile such as the PAHs, PCBs, and so forth, tolerate hydrogen more readily. If compounds are showing effects even at the lowest setting, use the offline process of Clean Only.

A



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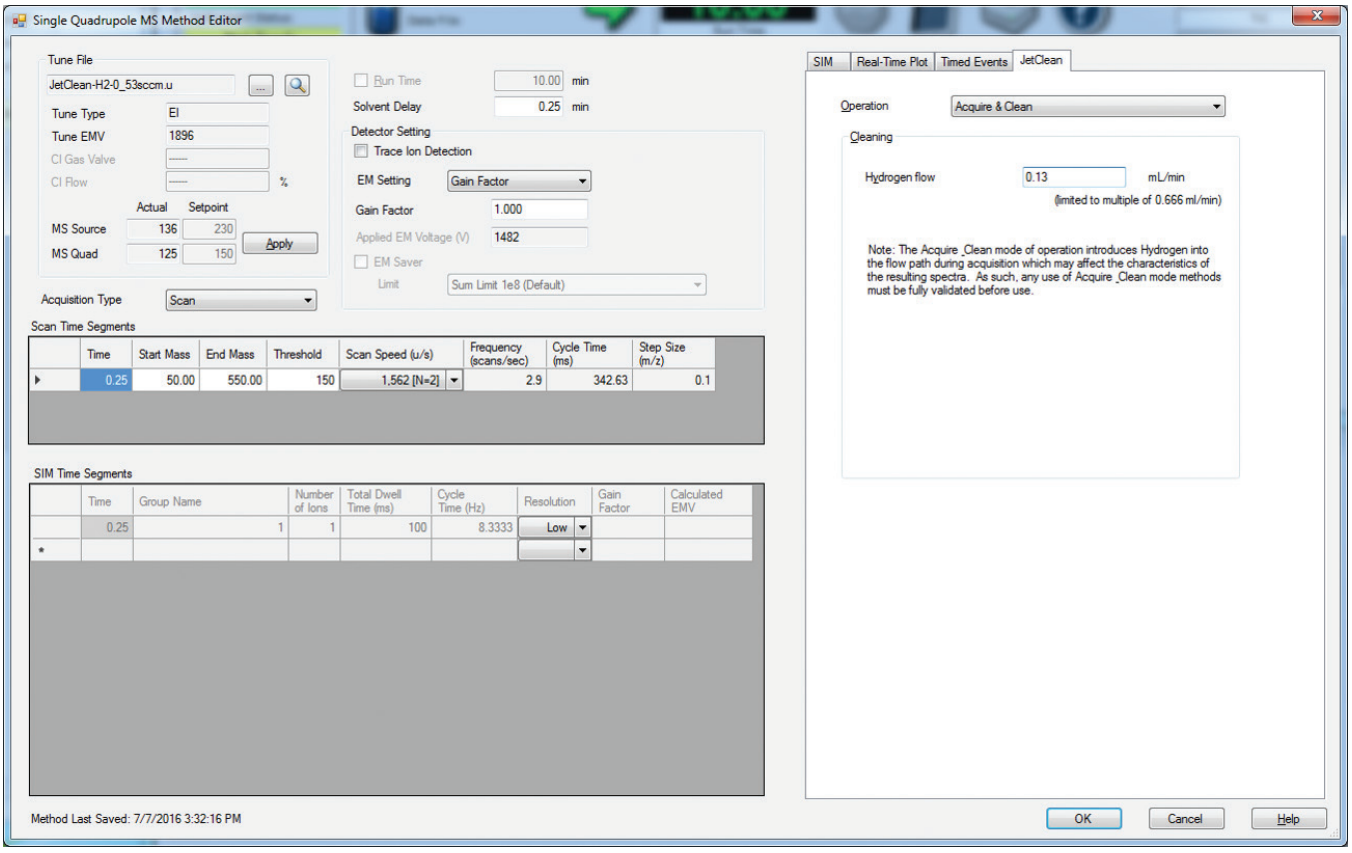


Figure 5. A) Acquire & Clean triple quadrupole. B) Acquire & Clean single quadrupole hydrogen flow setpoints.

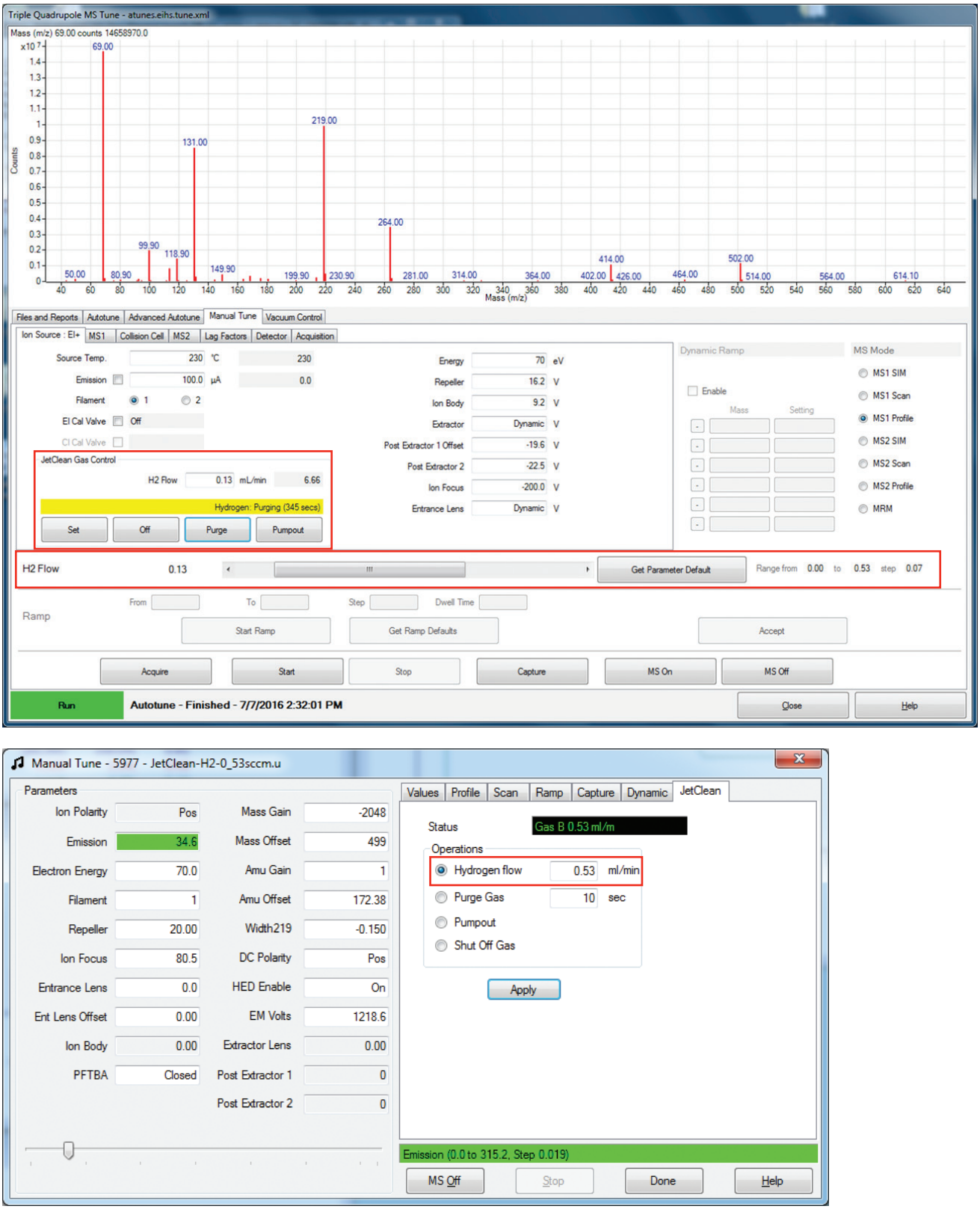
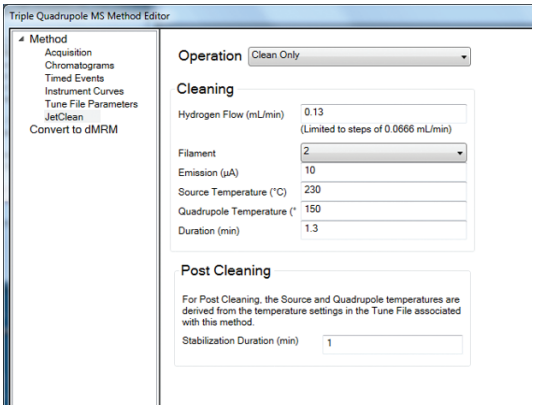


Figure 6. Acquire & Clean tune panels (TQ and SQ) hydrogen setpoint control.

Clean Only mode

This mode is universally applicable since hydrogenic species are generated outside the sample acquisition process. The sample acquisition GC/MS method can be converted to a Clean Only process method through the MS parameters panel. This leaves all GC zones as they are prior to an injection, but with Clean Only enabled, no injection is made as the GC injection method is automatically converted to Valve/Immediate Start. The method is then saved under a new name, preferably one that cites some JetClean conditions (for example: CleanOnly-25uA-H2-0_53sccm.M). This method can be run manually, or called in a sequence.

Figure 7 shows the JetClean parameters with Clean Only mode. Tables 1 through 4 show that there is a great deal of flexibility in these setpoints. The defaults represent a minimum starting point, and increasing any of these values represents a greater degree of treatment. Filament 2 is always the default filament to avoid additional stress to the first filament, the default acquisition filament. An exception is CI operation since there is only one filament. The emission defaults represent the very lowest possible settings, and would be the first parameters to increment for more extensive cleaning. For the HES source, the 10 µA setting will slowly reach stability over approximately one minute.



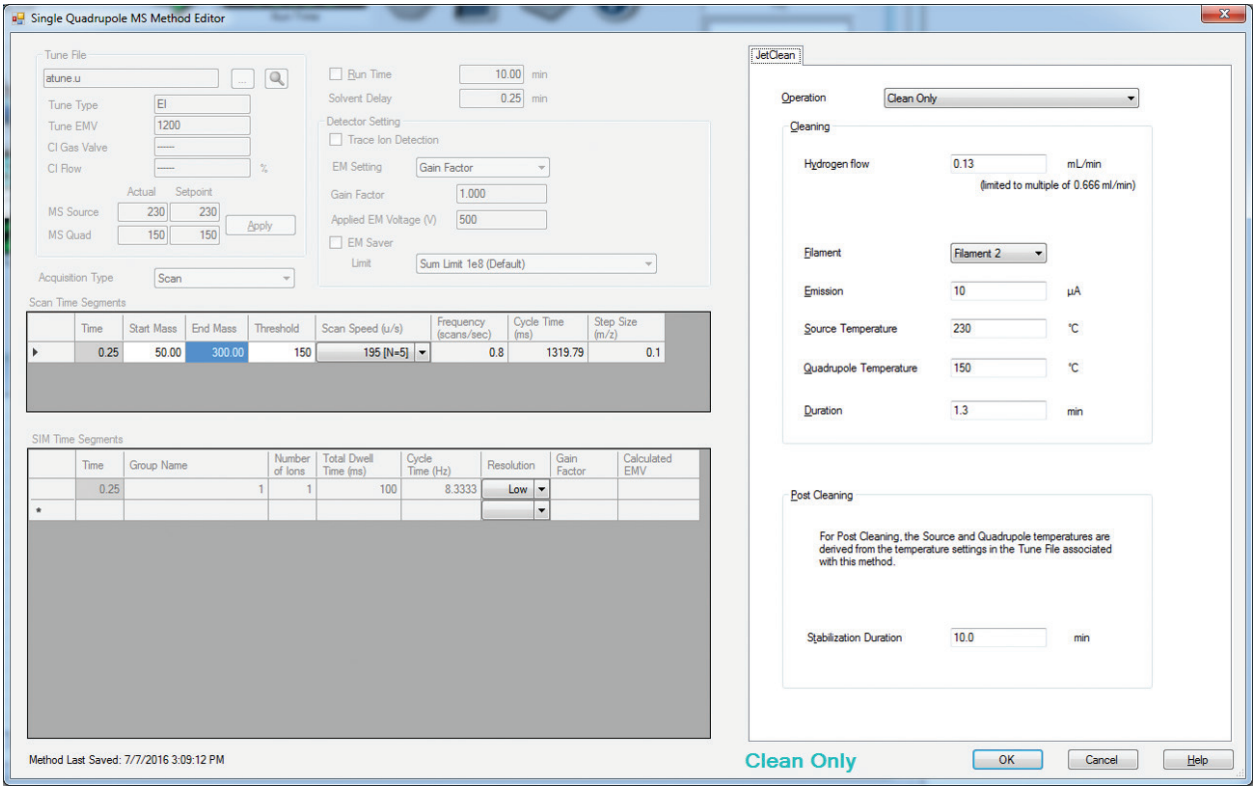


Figure 7. Clean Only TQ and SQ.

Setting a higher source temperature than that used in sample acquisition (that is, the standard tune file) is useful for more recalcitrant residues, but is not necessary in general and adds time to the process. Temperature does have an effect on the residues, but the hydrogen treatment process is very aggressive alone, as seen and described in Figure 8.

The strategy is to keep the times of treatment relatively short to fully realize the time savings of the JetClean system. The defaults represent an approach that could be applied quickly and frequently for light treatment. The flow and emission parameters can be increased to more rapidly and aggressively treat the source. An upper limit to the length of time dedicated to the process should be set, perhaps 10 or 20 minutes total. The solvent delay of 0.25 minutes is fixed and not editable. To increase the intensity of treatment, first increase the hydrogen flow and the emission to develop more aggressive conditioning. Avoid over-cleaning by studying the collected data, and comparing them to the performance of analytical standards.

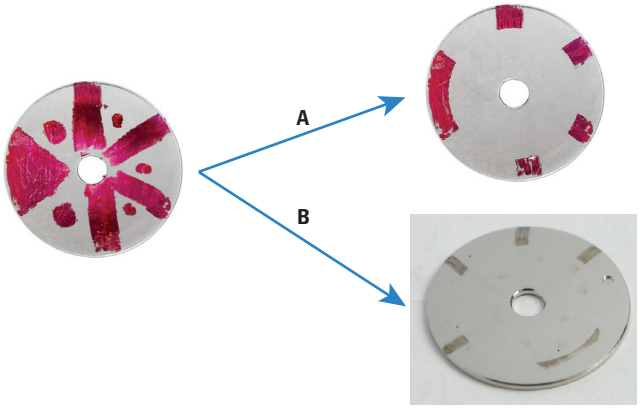


Figure 8. Removal of Rhodamine dye from an ion volume drawout lens under Clean Only processes at lower (A: 230 °C) and higher (B: 350 °C) source temperatures. The darkened color at the higher temperature (B) reflects that more thermal degradation has taken place. The unaffected areas are due to masking by other source elements, but the functional surface of the drawout lens has been restored.

In Clean Only mode, a data file is acquired during the treatment process as a record. Interpreting this record provides a great deal of insight into the status of the source, and how it is changing as the treatment is applied. The familiar MS parameters can be edited to record the data file, and these should be set before entering the Clean Only mode. Scan mode acquisition provides the most comprehensive record until ions that represent good indicators of the routine source contamination are discovered. If these ions are found, SIM is preferred. The upper end of the mass range need not extend pass a few hundred *m/z* (< *m/z* 500), with 300 *m/z* usually being sufficient. The usual lower end is 45 or 50 mass units. Starting the scan at mass 29 (TQ, with lowered mass cutoff of 30) or 28 (SQ) can be used to monitor hydrogen indirectly through the formation of N_2H^+ (*m/z* 29) to confirm that hydrogen is being applied. A number of unusual species formed and readily measured in SQ are H_3^+ (*m/z* 3), HeH^+ (*m/z* 5), ArH^+ (*m/z* 41), and so forth. The scan speed should be very low; one scan per second is adequate to keep the datafile small, and still record the changes in time. Figure 9 shows an example of such data. It is important to set the gain factor (GF) according to the scan range and source type: low GF if you include N_2 or N_2H, and an increased GF based on the species intensities seen in the scan window.

Extracting several ions shows that the onsets, apex, and kinetics of their intensities are not the same, as expected for a mixture of adsorbed components. It may be thought that the relative height of the EIC at any time reflects the degree of cleaning, meaning that when the ion current has fallen to half the initial or highest value, the source is 50% cleaned, or when down to 20%, it is 80% clean. Actually, the height of the initial signal can be proportional to how much hydrogen is present, and how high the emission current is set to (how much ionization), so the initial intensity is variable, as are the kinetics (as reflected in the shapes of the EICs). It is better to consider the area under the EIC versus time as indicative of the amount removed. Residues are removed in the order of physically adsorbed first and chemically adsorbed next. Hydrocarbons are rapidly removed, but water is difficult, not only because it is chemically adsorbed, but because there are large quantities of it (likely gram amounts) in the analyzer manifold. In general, the ion current will rise, then begin to fall to some asymptote. Trying to remove all signal at any *m/z* and create a pristine source will lead to problems (over-cleaning) and should be avoided.

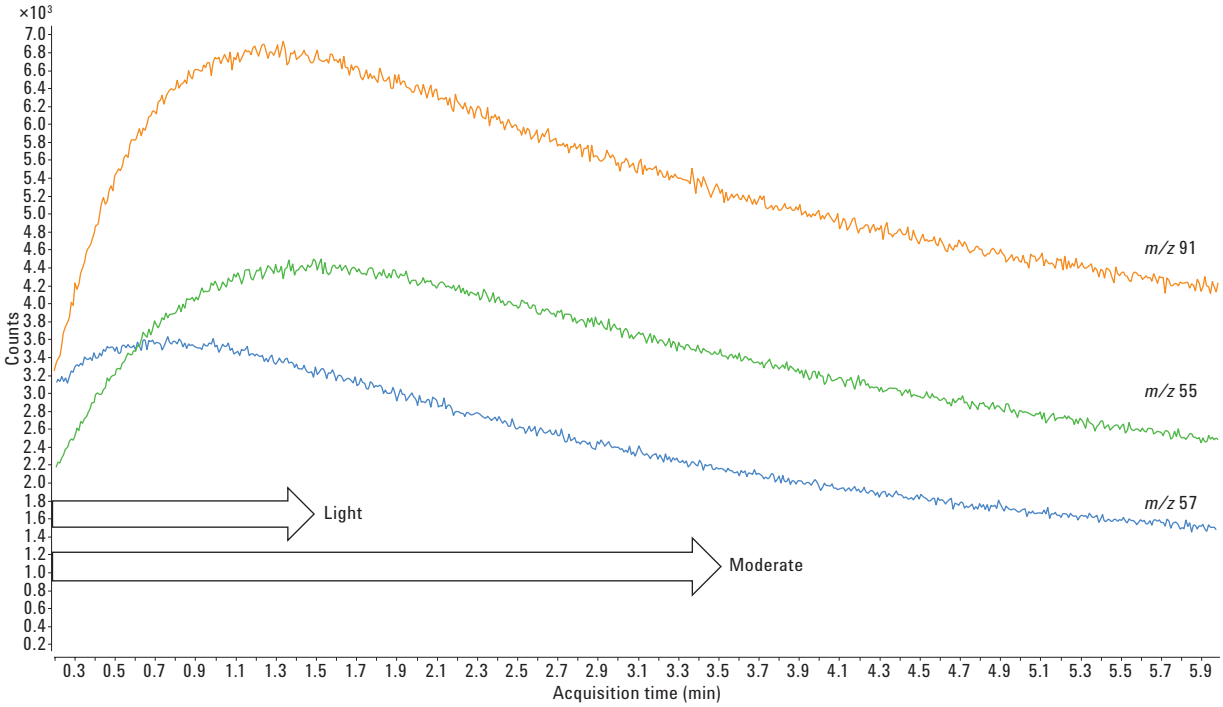


Figure 9. EICs for Clean Only JetClean for the Agilent 5977B SQ-HES over the range of 0 to 6 minutes.

Figure 10 shows the EIC for *m/z* 57, both as absolute and normalized, on a relatively clean, artificially-fouled source under several hydrogen flow settings but a single (10 µA) emission. In the absolute EIC, the suppression of the intensity is a source phenomenon: as the hydrogen flow increases, it gets crowded in the source. So the highest flow is actually removing more material per unit time, and reaches an asymptote rapidly. In the normalized view, notice that the time required for the EIC height to drop to 0.25 is shortest for the highest flow setting, and increases as the flow decreases. Also note that the asymptote for this material is achieved rapidly under these conditions (remembering that higher flow and emission may reveal more). Other agents are more difficult to remove, and worse, they may not have a good ion to track.

It is recommended that the Clean Only method first be executed manually and that the TIC (or EIC) trace is followed, and the method stopped before the trace has flattened out (that is, reached the asymptote). This will help develop a fixed method for the source treatment as parameters are adjusted and a fixed number of samples are run.

As with manual cleaning, after the source is treated, it should be stabilized, then conditioned. A stabilization time is selectable up to 2 hours. One approach is a relatively rapid Clean Only method (<20 minutes), followed by a bake out, then a stabilization time of a few hours such as the typical vent and clean process. This is followed by retuning, or a gain factor update, and some injections to condition the source. Water plays a very important role in the MS, and it needs to re-equilibrate inside the source and manifold.

In SQ systems, these steps can be automated in a standalone sequence (for example, Source-JetClean.S) that can be executed when needed, or added to a sample sequence for execution prior to or following a sample batch. The BAKE command is configured in the Tune View, and 60 minutes is recommended for equilibrium time; otherwise, the SLEEP command can be used to add time. The BAKE command is not currently supported in TQ systems.

Default methods are found in the directory: methods\default for a JetClean-enabled GC/MS system, and can be loaded and used as starting points. It is recommended that monitors be added for the JetClean process so that the desired setpoints can be witnessed. These monitors are very useful for viewing the status of the system and all important zones and parameters. For Clean Only, settings such as emission, hydrogen flow, and EM voltage can be checked. In the TQ, MS actuals and setpoints can be monitored during operation through the MS Status panel (note: hydrogen is automatically shut off after 10 minutes of inactivity if the default timeout setting is not altered).

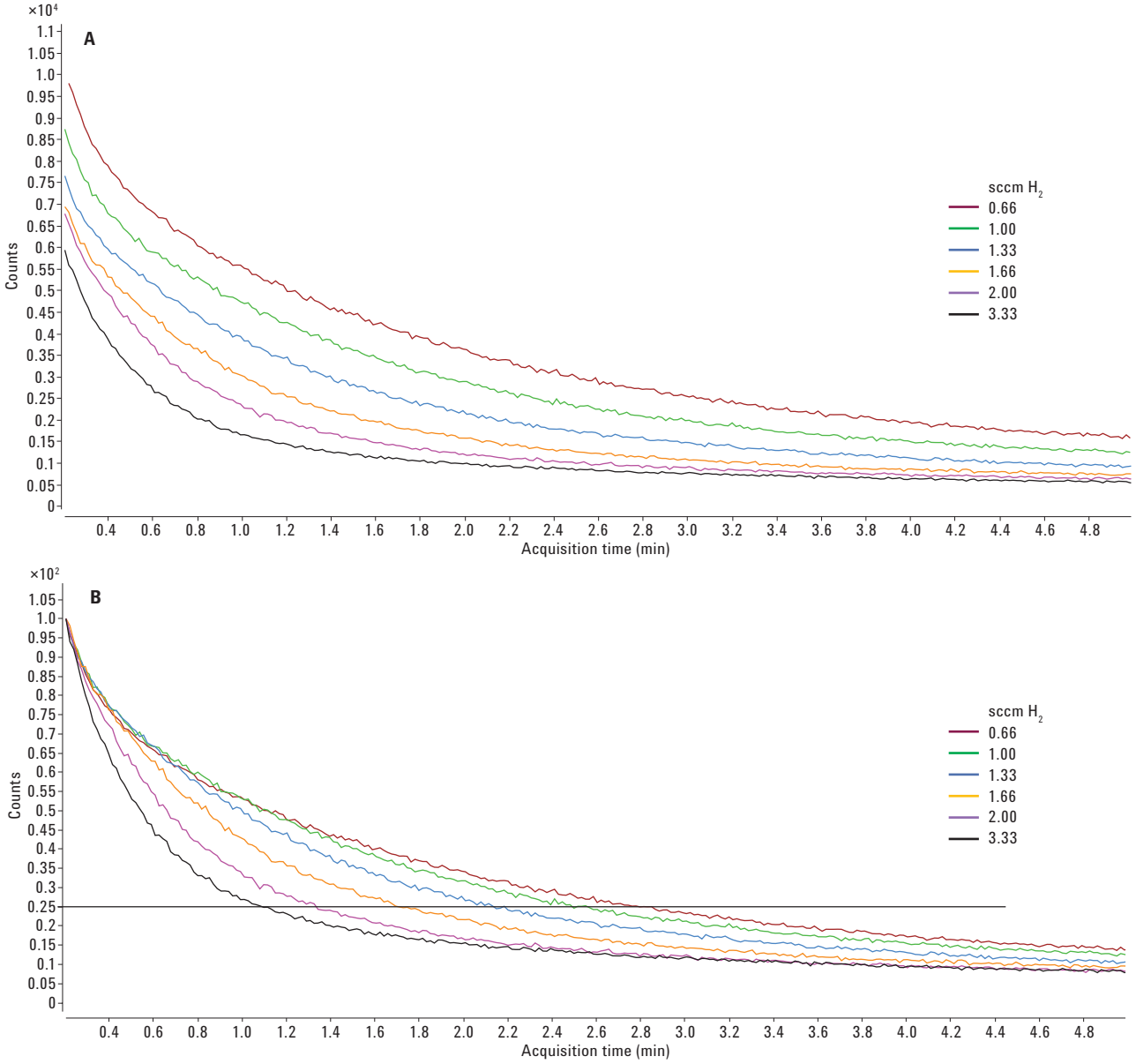


Figure 10. A) Clean Only mode: EIC for *m/z* 57 at six different H_2 flow setpoints (10 µA). B) Normalized EIC for *m/z* 57 at six different H_2 flow setpoints (10 µA). A line at 25% has been extended for clarity.

Method remarks: Integrating Agilent JetClean advantages

It may be useful to explore other source parameters and those of a standard operation. Typically, the highest source temperature possible is used during GC/MS acquisition. This is meant to keep the source clean, and provide a robust operation, although unfavorable aspects such as increased compound fragmentation may occur. However, through JetClean, the source condition can be more easily maintained so that the source temperature for sample acquisition methods may be lowered, thus providing more favorable responses or ion ratios for fragile compounds.

Conclusion

Agilent JetClean is a flexible approach to avoiding the process of manually cleaning the ion source in a GC/MS. It enables the development of nearly automatic, sequence-driven source cleaning and conditioning. It is important to recognize that source stability is being sought and not absolute response. The user can always increase the gain factor. Some sources produce a very high response that drifts (a typical, but unfavorable condition) before the system has stabilized. This final stability can be generated several ways already familiar to the user, such as bake out and wait, sample injections, analyte protectants, and so forth. The Acquire & Clean mode can be applied to greatly enhance the longevity and stability of source performance where compound chemistry permits. Complementary to that online process is the globally applicable Clean Only mode, which is independent of the analysis. With these two methods, the time between manual cleanings of an ion source can be extended. Proper JetClean operation yields greater instrument up-time with better analytical results.

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