The 5975C Series MSDs: Normalized Instrument Tuning

Technical Overview

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Introduction

The automated optimization of ion detection in a mass spectrometer, commonly referred to as "autotuning," has been a tremendous simplification in MS operation. This critical operation has become so routine that it is taken for granted. To perform a tune or autotune, MS systems introduce a volatile calibrant and adjust the MS parameters to meet some criteria, such as the abundances of certain calibrant ions. Historically, that is how the 597X Series of instruments have been tuned. (Software allows the user to change or adjust these tuning targets through the Tune Wizard.)

After the ion optics have been optimized and calibrant ion peak widths adjusted, the target calibrant fragment ion abundances are achieved by adjusting the voltage applied to the electron multiplier (EM). The voltage applied across the EM amplifies the very small electron current emitted from the high-energy conversion dynode (which has converted the ions emanating from the mass filter to electrons) to produce a much larger current—the target signal abundances.

A measure of the degree of amplification of this very small current to the higher, more easily quantified current is called the multiplier "GAIN." This process produces an electron multiplier voltage (EMV) based on the target calibrant ion abundances in the source, which is derived from the relatively high pressure of the calibrant gas perfluorotributylamine (PFTBA). Because the analyst is usually interested in determining compounds at very low levels, the habit is to add an additional incremental voltage upon that obtained in autotuning on the calibrant (for example, ATUNE.U + 400V). This produces a GAIN more appropriate to trace analysis and is reflected in higher signals than the case where the ATUNE.U voltage is used alone.

A far superior approach is to adjust the multiplier voltage setting to produce a particular GAIN, which is implemented in the 5975C MSD.

The advantages of this are:

- Better consistency for compound responses. After a source cleaning, column servicing, or EM replacement, an instrument retuned to the same GAIN as previously used will show compound responses more similar to and more consistent with those obtained prior to maintenance. Aging of detector EMs is always an issue, and acquiring under a fixed GAIN is a better way of ensuring that analyte response remains reproducible.
- Better agreement between different instruments for the same compounds. If instruments are tuned with the same criteria and to the same GAIN, they will show better agreement in compound responses among the instruments. Tuning against abundance alone and then adding another voltage to produce the sensitivity required assumes that the multipliers involved have identical or similar GAIN curves. This is very seldom true.

- Better diagnostics in tuning and troubleshooting. For example, more exacting water and air criteria can be developed by tuning to a particular GAIN and then examining the air and water background. When inspecting a chromatogram acquired under a fixed GAIN, it becomes easier to decide whether column bleed profiles have increased or decreased over time. Further, during tuning as the voltage applied becomes too high to reach a fixed GAIN value, it is clear that the EM has reached the end of its life. And most importantly, if compound responses before and after servicing or even just between tunes are not similar, this indicates that there is likely a problem in the GC portion of the GC-MSD that needs attention. This is invaluable for establishing operation criteria.

To understand these benefits it must be realized that the change in the GAIN as the voltage of the EM is changed is NOT linear nor all that consistent between EMs. Meaning if the EMV is increased by 100 V, the multiplier does not increase in any direct proportion and in fact is nonlinear and a function of the voltage range involved. In other words, say two different multipliers each "tune" or "autotune" at nearly the same voltage (say 1,300 V). Adding 400 V to each of them produces the same voltage (for example, 1,700 V) but *not* usually the same GAIN nor the same signal or responses for the analytes. But if both EMs are adjusted to the same GAIN, then both signals and compound responses should be the same. In fact, if they are very different, it means that the signals reaching the detector are different. This is due to problems such as the GC and inlet needing servicing so that the same amounts of analyte reach the source or that the source needs to be cleaned so that it is more efficient and other possibilities as above. This is why normalizing to a particular GAIN is important and valuable.

This document provides an introduction to the implementation of the GAIN normalized tuning on the ChemStation G1701EA (E.00.xx) software and recommendations for its use. This software is standard for the new 5975C MSD, and data shown in this overview were gathered on that platform.

Gain Normalization in the ChemStation Software

Figure 1 shows the additional tuning option added to the Tune menu in the *Tune and Vacuum Control View*. The additional command *Gain AutoTune* (*Atune.U+HiSense.U*) executes a GAIN normalized tune that creates two files: ATUNE.U and HiSense.U. The ATUNE.U is the standard AutoTune file in every respect except that the EMV is set to obtain a GAIN of 10^5 (as seen in the Tune report, lower right corner as EM Gain). The other tune file created, HiSense.U, has the EMV set to

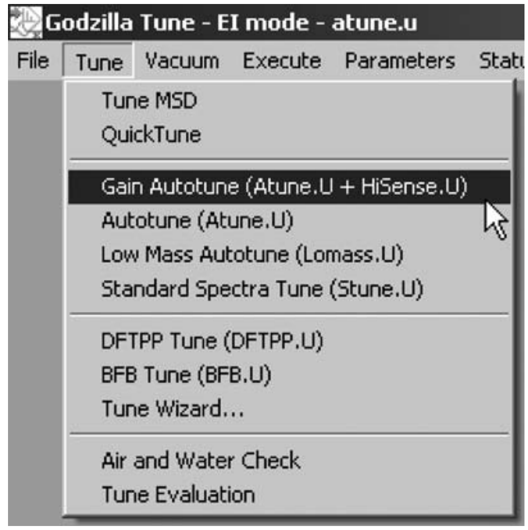

Figure 1. **Gain normalization tuning menu command.**

obtain a GAIN of 15 x 10^5, or 15 X higher than the standard ATUNE setting.

Another approach to GAIN normalizing tunes is provided in the menu under *Execute\EM Gain Normalization* (Figure 2). With a Tune loaded (for example, mytune.U), applying one of the first three menu choices generates EMVs with GAIN values set as 1 x 10^5, 10 x 10^5, or 15 x 10^5, respectively. If ATUNE.U is the loaded file, the file is renamed with an extension *ATUNE_10X.U* or *ATUNE_15X.U* where X is a substitute for 10^5. (Applying a GAIN normalization of 1X or 10^5 just creates the standard ATUNE.U so no extension is added). Selecting the lowest radio button creates the HiSense.U file.

EM Gain settings are saved with the tune so that if the menu command TUNE is executed, the tune applies all settings and then adjusts the EMV to meet the previously assigned GAIN. (This is the uppermost item in the pull-down menu of Figure 1). GAIN values are given in the tune reports.

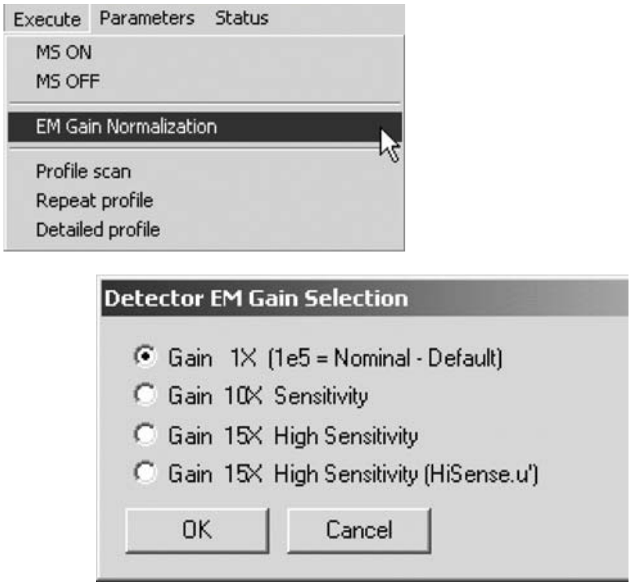

Figure 2. **Applying EM gain normalization.**

Suggestions on Applying GAIN Normalization

In the past, users would create an ATUNE.U and in their method add about 400 V to the tune in the MS Parameters panel (Figure 3, left panel). This would create an EM Gain of about 10 x 10^5 to 15 x 10^5, depending on the multiplier, its history, etc., and proved widely useful for trace analysis. Instead of this procedure, we recommend simply assigning the HISense.U file and *not* adding any incremental voltage so that the EMV is exactly as obtained in the tune file (Figure 3, right panel).

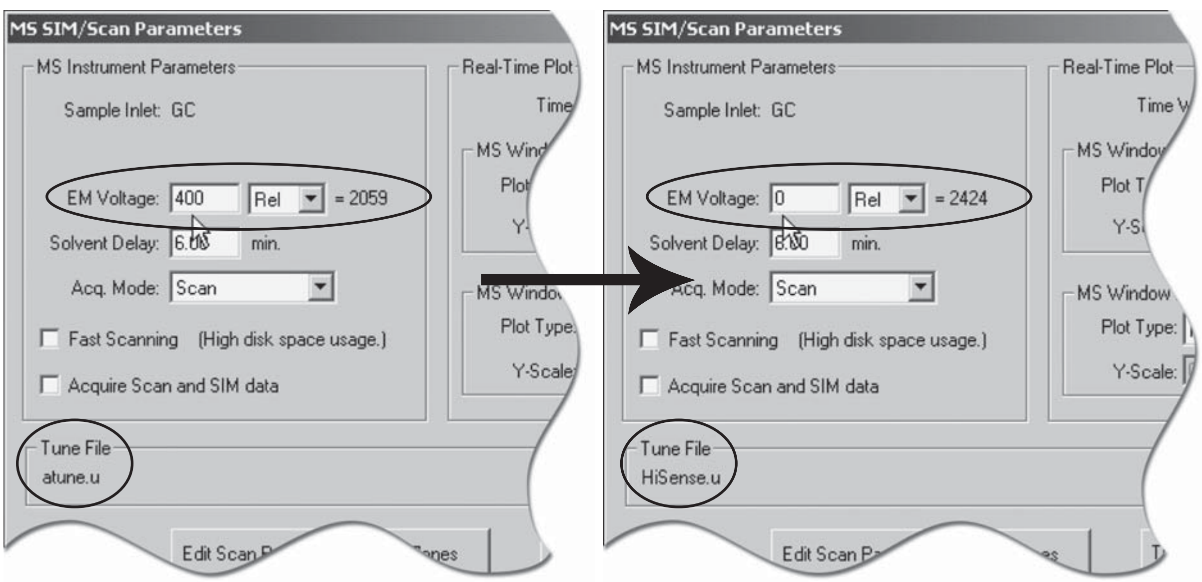

Figure 3. **Recommended MS Parameters EM settings and tune file changes.**

Frequently Asked Questions About the Effects of EMV Settings and GAIN

What effects would I see on my compound responses for the various EM Gains?

As you would expect, this depends on the particular multiplier in the instrument and its history. But to a rough approximation, the compound responses will follow the GAIN. Figure 4 shows an overlay of the RTICs of the four hexachlorocyclohexanes acquired under four different EM Gains. They stack up in the order one would expect: lowest is the ATUNE.U+0V or EM Gain 1X (10^5); next, ATUNE+400V, which is close to EM Gain 10X (10×10^5); and the highest is obtained with the HiSense.U, which always has GAIN set to 15X. Notice that the baseline and signal follow this pattern.

What EM Gains should I choose for my analysis?

This should be explored by the analyst for his or her particular application but, as general guidance, if trace analysis is being pursued (analyte amounts < 1ng), then the HISense.U is the best approach. However, if higher concentrations are involved (> 1 ng), then lower EM Gains will be more successful, such as ATUNE.U or intermediate between this and ATUNE_10X.U.

Why should I not just apply a lot of voltage to the EM and use a very high EM Gain?

If the concentrations are high, the signal will saturate the detector and chromatographic peaks will have a flat top and linear working ranges will become very small. But the user can demonstrate by experiment that a balance must always be struck between signal and noise and that beyond a GAIN of the HiSense.U tune, the signal-to-noise ratio will not improve but the linear working range will begin to collapse. Interestingly, on the other end, the lowest GAIN setting of Figure 4 produces the highest signal-to-noise! This is because even though the signal is low(est), the noise is also very low as can be seen by the baseline. So why not run the EMV and GAIN as low as possible?

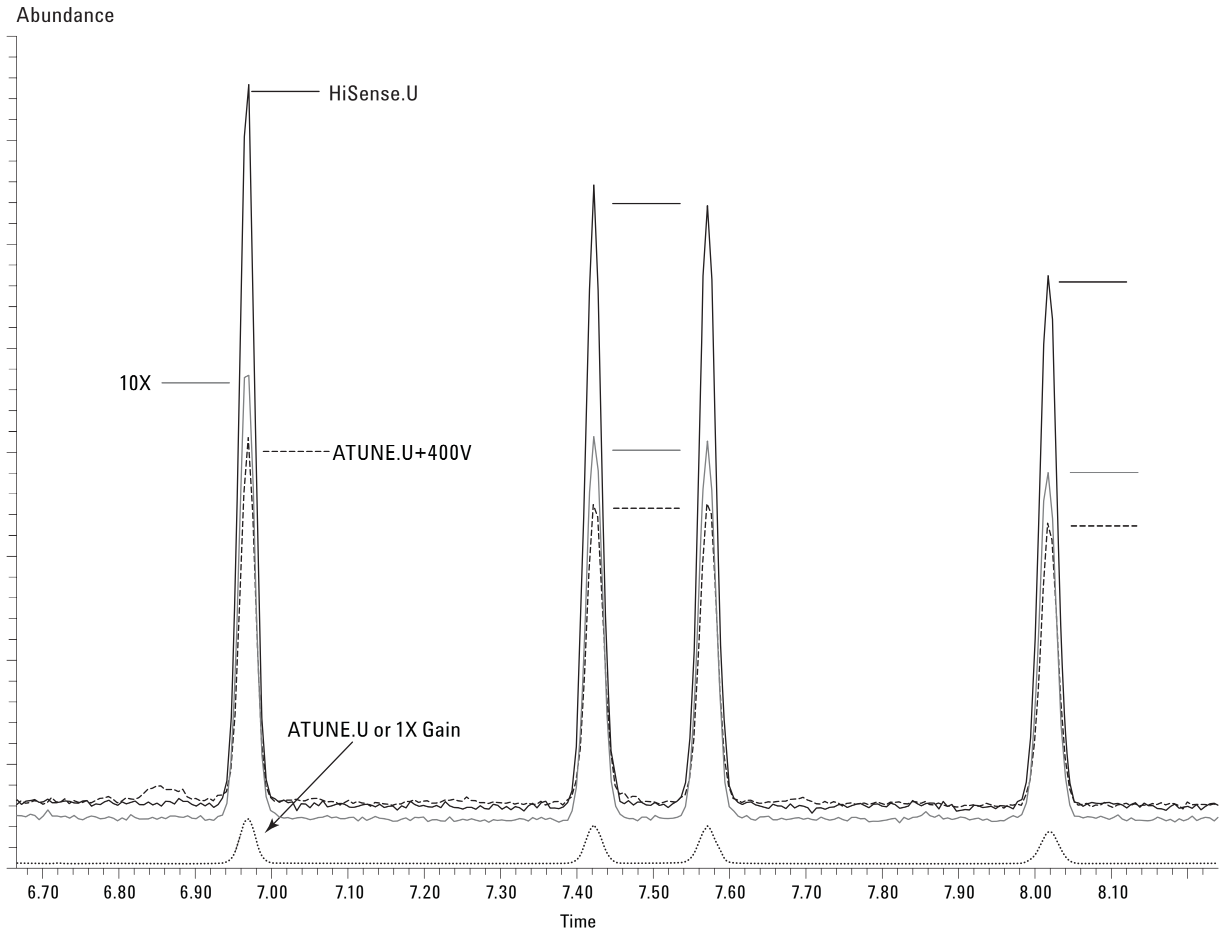

Figure 4. Responses at several EM Gain settings.

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