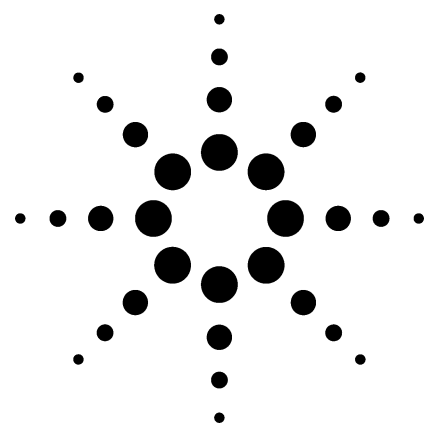


BFB Tuning for Environmental Analysis: Three Ways to Succeed

Application

Environmental



Author

Philip L. Wylie
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808-1610
USA

John E. Pellerin
Agilent Technologies, Inc.
40 Shattuck Road
Andover, MA 01810
USA

Abstract

The United States Environmental Protection Agency methods 524.2, 8260B, and Contract Laboratory Program Statement of Work employ purge and trap concentration of volatile compounds in water samples with analysis by gas chromatography/mass spectrometry. Each method requires the mass spectrometer to meet specific tuning criteria before proceeding to actual samples. This paper summarizes these tuning criteria, and shows three different ways that the Agilent Technologies 6890/5973 gas chromatograph/mass selective detector system can be tuned to meet them. A very simple and robust procedure is described in the Modified Autotune section. A quick reference guide for this procedure is given at the end of the paper under Modified Autotune Summary.

Introduction

If you are already familiar with 4-bromofluorobenzene (BFB) tuning and evaluation procedures, you may want to go directly to the section titled “Modified Autotune Summary” found at the end of this paper. It offers an alternative approach for tuning Agilent 6890/5973 GC/MSD systems that is routinely successful in this laboratory.

The United States Environmental Protection Agency (USEPA) has developed several methods for the analysis of volatile organic compounds (VOCs) in water samples. The three most widely used procedures all employ purge and trap (P&T) sample introduction followed by capillary column gas chromatography with mass spectral detection (P&T/GC/MS). USEPA Method 524.2 revision 4¹ is used for drinking water analysis while Method 8260B revision 2² is used for wastewater. The USEPA Contract Laboratory Program Statement of Work (CLP-SOW)³ uses a similar P&T/GC/MS method for the analysis of hazardous waste.

There are many similarities among these three USEPA volatiles methods. One common requirement is that the GC/MS system must be tuned in such a way that 4-bromofluorobenzene (BFB) meets specific ion abundance criteria. This requirement helps to ensure that data are comparable between instruments of different design and



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among various laboratories. This paper summarizes USEPA method 524.2, 8260B, and CLP tuning criteria, and shows three different ways that the Agilent Technologies 6890/5973 GC/MSD system can be tuned to meet them.

Experimental

A standard containing fluorobenzene, 1,2-dichlorobenzene- d_4 , and 4-bromofluorobenzene at 2.0 mg/mL was purchased from AccuStandard (New Haven, CT). A portion of this solution was diluted in methanol (B&J HPLC and pesticide grade) to a concentration of 50 ng/ μ L.

Standards for tune evaluation were injected by syringe or P&T into several different Agilent Technologies 6890/5973 GC/MS systems. When making syringe injections into the split/splitless inlet, a liner with a 900- μ L volume was used and no more than 1.0 μ L was injected to avoid over-expansion in the inlet.

Results and Discussion

Tuning Criteria

Table 1 lists the tuning criteria for USEPA methods 524.2, 8260B, and CLP-SOW. All three methods base their tuning criteria on the ion responses of BFB. All ion responses are reported relative to m/z 95, which is assumed to be the base

peak even though ions 174 and 176 may be larger in the CLP-SOW method.

While many of the requirements in Table 1 are the same for all three methods, some important differences are worth noting. Method 8260B actually allows the analyst to use the tuning criteria specified in either of the other two methods. More importantly, it allows one to use “manufacturers tuning (sic) instructions” so long as it does not hurt method performance. However, many laboratories still follow the BFB tuning requirements specified in method 8260B or choose to substitute CLP-SOW tuning criteria.

Methods 524.2 and 8260 require that m/z 95 be the base peak in the BFB spectrum, which caps the m/z 174 relative abundance at 100% (relative to m/z 95). The CLP-SOW requirements allow m/z 174 to be up to 120% of m/z 95. Tuning procedures that reduce the response of m/z 174 too much may lead to lower overall sensitivity, especially for bromoform which has a quant ion of m/z 173. Conversely, maximizing this ratio, within the requirements of the method, can enhance overall sensitivity.

Automated BFB Tuning

The Agilent 5973 MSD uses perfluorotributylamine (PFTBA) for electron impact tuning because it exhibits good stability, the right volatility, and a wide range of fragment masses. However, USEPA volatiles methods evaluate the tune using BFB which produces an entirely different spectrum.

Table 1. Criteria for BFB Tuning for Three Capillary GC/MS Volatiles Methods

Mass (m/z)	Relative Abundance Criteria		
	Method 524.2	Method 8260B ^a	CLP-SOW
50	15 to 40% of 95	Same as 524.2	8 to 40% of 95
75	30 to 80% of 95	30 to 60% of 95	30 to 66 % of 95
95	Base Peak, 100%	Same as 524.2	Same as 524.2
96	5 to 9% of 95	Same as 524.2	Same as 524.2
173	<2% of 174	Same as 524.2	Same as 524.2
174	>50% of 95	Same as 524.2	50 to 120% of 95
175	5 to 9% of 174	Same as 524.2	4 to 9% of 174
176	>95 to <101% of 174	Same as 524.2	93 to 101% of 174
177	5 to 9% of 176	Same as 524.2	Same as 524.2

^aAlternative tuning criteria may be used (for example, CLP or Method 524.2) including manufacturer's instructions provided that method performance is not adversely affected.

Therefore, automated (or manual) tuning procedures must adjust PFTBA ion responses in order to get the desired BFB response ratios. Agilent G1701CA EnviroQuant ChemStation software automates BFB tuning so that the instrument typically passes the more restrictive USEPA Method 524.2 and 8260B requirements listed in Table 1. After tuning, the analyst must inject a BFB standard by syringe or P&T to verify that the tune passes the requirements for the method in use.

Automated BFB tuning adjusts MSD source parameters so that PFTBA ion abundances meet predetermined “targets.” The default PFTBA target values are set so that a subsequent BFB injection should meet the requirements for all three methods. Table 2 shows a portion of a BFB tune report that includes the target responses (as a percentage of m/z 69) for m/z 50, 69, 131, 219, 414, and 502. The actual abundances achieved by the tune are shown on the last line. When these targets

Table 2. A Portion of a Typical BFB Tune Report

Target Mass:	50	69	131	219	414	502
Target Abund (%):	1.0	100.0	45.0	55.0	2.4	2.0
Actual Tune Abund (%):	1.2	100.0	48.1	59.3	2.7	2.3

are met, the Agilent 5973 MSD normally passes any of the tuning criteria listed in Table 1.

Figure 1 shows an average spectrum obtained for a 1- μ L manual injection of BFB (50 ng/ μ L split 50:1) using the tune shown in Table 2. Agilent G1701CA EnviroQuant ChemStation Environmental Data Analysis software can evaluate the spectrum automatically and generate a report that is archived with the data file. Because BFB tuning criteria are not uniform among USEPA methods, the analyst must first specify the allowable ranges using the form shown in Figure 2. The form is accessed in Environmental Data Analysis by selecting Tuner/Edit BFB Criteria on the dropdown menu.

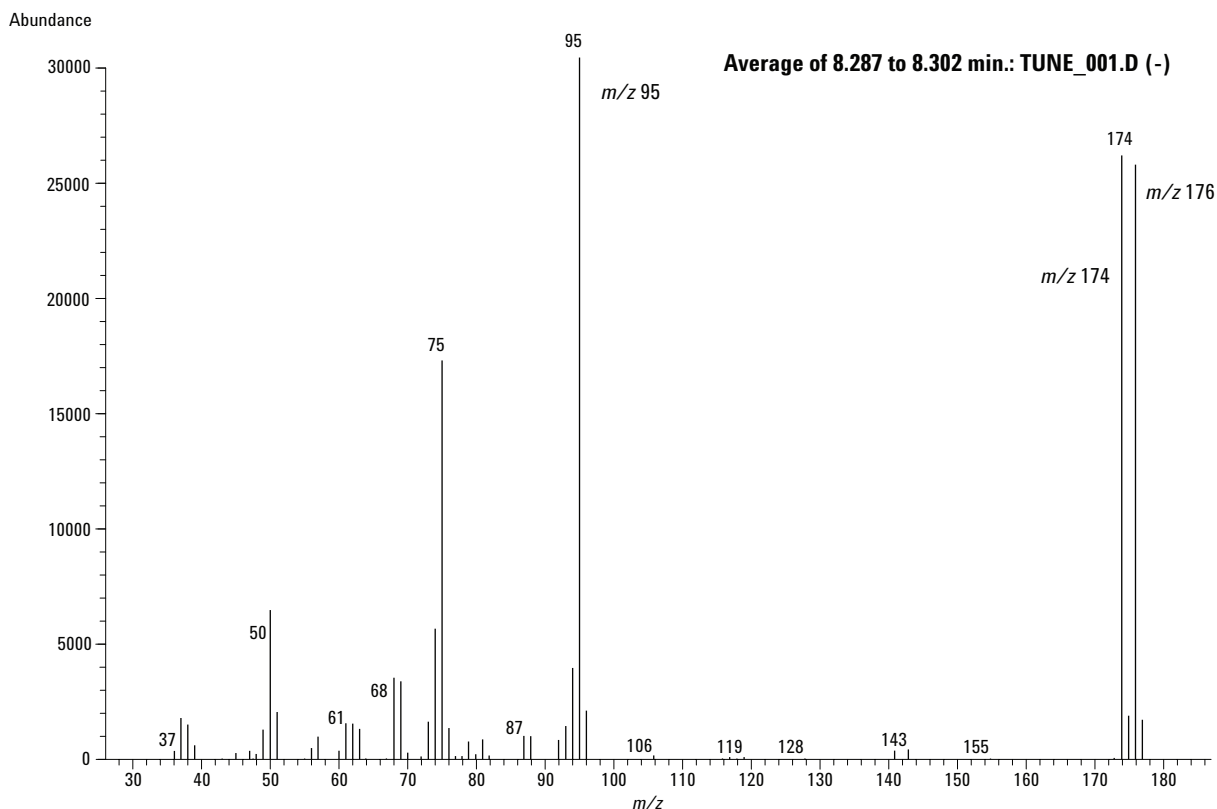


Figure 1. Average spectrum of BFB after performing a standard BFB automated target tune. One μ L of a methanol solution containing 50 ng/ μ L of BFB was injected by hand.

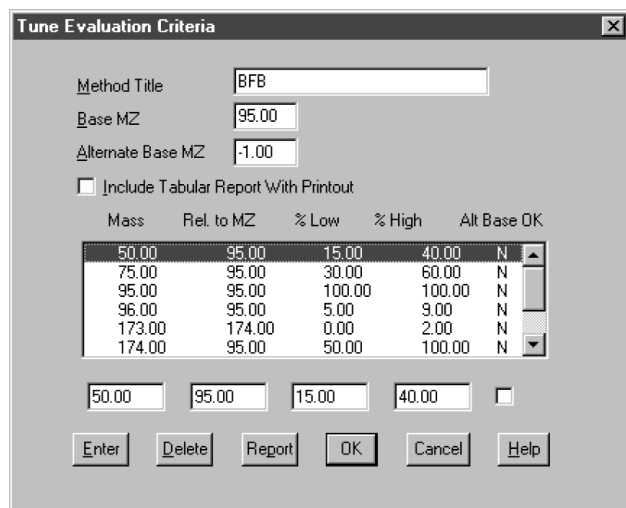


Figure 2. The Agilent G1701CA EnviroQuant ChemStation screen for entering BFB tune criteria. The user can modify the parameters to meet the requirements of the method in use. These values are used by the ChemStation for automated tune evaluation.

Having entered abundance criteria for the method in use, one can automatically assess the suitability of the tune using the EnviroQuant software (Figure 3). One can choose to "Evaluate BFB to Screen/Printer" in which case it will evaluate the current spectrum. This can be a single spectrum or an average. Alternatively, by choosing "Autofind BFB to Screen/Printer," the software automatically finds BFB in the chromatogram, averages the top three spectra and subtracts a baseline spectrum. In either case, a report such as the one in Figure 4 is generated. The most recent report is archived in the datafile.d directory in a file called tuneeval.txt.

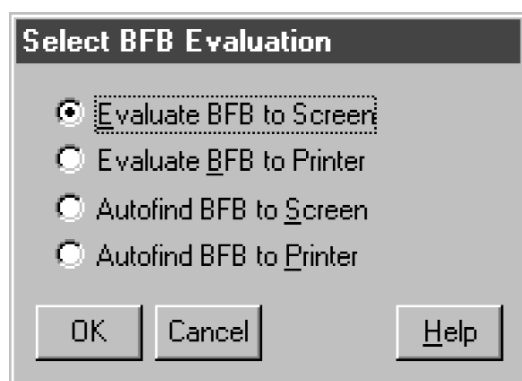


Figure 3. Choices for automated BFB tune evaluation by the EnviroQuant software. The "Evaluate BFB..." choices use the spectrum (single or averaged) in Data Analysis window 1 for evaluation. The "Autofind..." choices automatically find the BFB peak, average the top three BFB spectra and subtract a baseline spectrum prior to evaluation.

BFB

Data File : C:\HPCHEM\1\DATA\Sep24_01\TUNE_001.D Vial: 1
 Acq On : 24 Sep 2001 2:25 pm Operator:
 Sample : BFB for tuning 1 uL Inst: GC/MS Ins
 Misc : Multiplr: 1.00
 MS Integration Params: rteint.p

Method : C:\HPCHEM\1\methods\envdef.m (RTE Integrator)
 Title :

AutoFind: Scans 1567, 1568, 1569; Background Corrected with Scan 1559

Target Mass	Rel. to Mass	Lower Limit%	Upper Limit%	Rel. Abn%	Raw Abn	Result
50	95	15	40	21.6	6769	PASS
75	95	30	60	56.5	17708	PASS
95	95	100	100	100.0	31317	PASS
96	95	5	9	7.1	2209	PASS
173	174	0.00	2	0.0	0	PASS
174	95	50	100	82.8	25933	PASS
175	174	5	9	7.4	1910	PASS
176	174	95	101	99.3	25747	PASS
177	176	5	9	6.6	1702	PASS

TUNE_001.D envdef.m Mon Sep 24 16:00:27 2001 MSVOC04

Figure 4. The Agilent EnviroQuant ChemStation BFB Tune Evaluation Report for the spectrum shown in Figure 1.

In this case the automated BFB tuning procedure produced a tune that passes Method 524.2 and 8260B criteria with a 174/95 ratio of 82.8%. This ratio is limited to 100% by these USEPA methods, which specify that m/z 95 must be the base peak. To meet these strict guidelines, one has to "de-tune" the Agilent 5973 MSD which results in somewhat lower instrument sensitivity. Laboratories may want to increase the 174/95 ratio so it more closely approaches the 100% limit of Methods 524.2 and 8260B or so that it approaches the 120% limit specified in the CLP-SOW method. Most laboratories that perform Method 8260B tune their instruments to meet the CLP-SOW requirements because the method allows laboratories to use these tune criteria and the MSD performance is closer to optimum.

In addition to the automated BFB tune, there are two procedures that can be used to improve instrument sensitivity, to meet the more liberal CLP-SOW requirements, or to create a passing tune should the standard BFB autotune fail. In this laboratory, the "Modified Autotune" procedure was found to produce tunes that routinely passed BFB criteria for any of the three methods. As shown below, changing the BFB tuning targets can also produce a passing BFB tune while enhancing the signal for bromoform.

Target Tuning

Automated BFB tuning adjusts MSD source parameters to achieve the target responses required for the method in use. This is essentially a "target tune" procedure where the initial target abundances provided by the software are designed to

meet the more restrictive 524.2 and 8260B requirements. When needed, it is easy to change the target PFTBA relative abundance criteria to produce the desired affect on the BFB ions. This is done by selecting View/Manual Tune/Set Tune Targets.

For example, consider the spectrum in Figure 1 which passed all of the tuning criteria, but which had a lower than optimum m/z 174 response. Experience in this laboratory has shown that increasing the relative abundance of m/z 174 will increase the overall sensitivity of the instrument, in particular for the bromoform response at m/z 173. As shown in Figure 5, the target abundances for ions 131 and 219 were each increased to 70% from their default values of 45% and 55% respectively. These choices were saved to the BFB.U tune file and a new BFB Target Tune was run. Figure 6 shows the new BFB spectrum (average of three spectra across the apex with baseline subtraction) which passes CLP-SOW criteria (Table 1) and is, therefore, satisfactory for either CLP or 8260B volatiles methods.

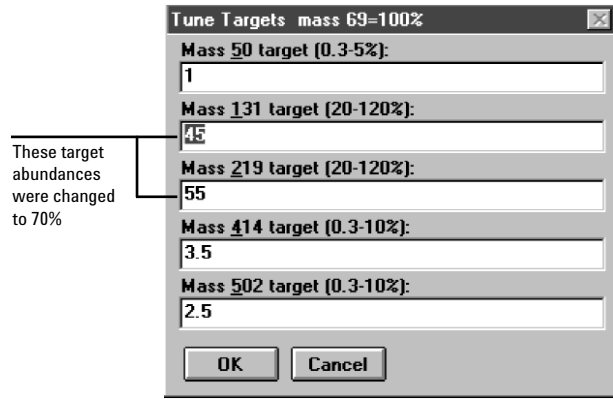


Figure 5. PFTBA target abundance values (relative to m/z 69) used for "target" tuning. When these abundances are saved to the BFB.U tune file, they are used by the BFB target tune algorithm.

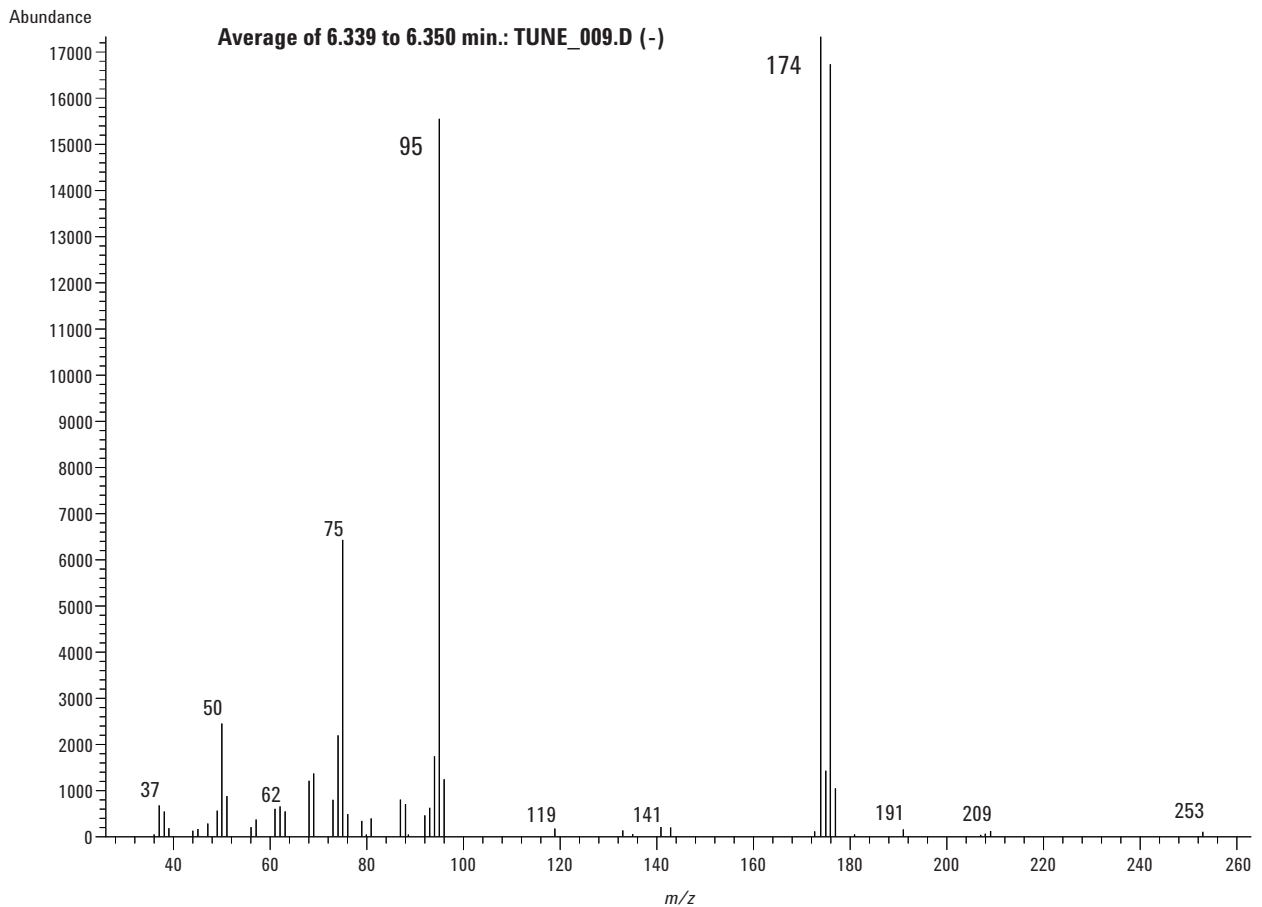


Figure 6. Average BFB spectrum obtained by changing the tune targets for m/z 131 and 219 to 70% (relative to m/z 69). This spectrum passes CLP-SOW tuning criteria.

Modified Autotune

With the convenience of automated tuning procedures available in the Agilent ChemStation software, most analysts have gladly given up the idea of manually tuning their 5973 MSDs. A combination of automated tuning with a slight manual modification has given excellent BFB results in this laboratory. The total process is easy and usually takes just a few extra minutes after the autotune is complete. The steps are described below and are summarized in a “quick reference” format in the next section.

1. From the Manual Tune portion of the software, perform an Autotune (select Tune/Autotune). This algorithm tunes the Agilent 5973 MSD for maximum sensitivity over the entire mass range and is widely used by methods that do not specify other tune criteria. This autotune emphasizes overall sensitivity by improving abundances for higher mass ions (for example, 502). As a result, the Autotune procedure typically gives an abundance for m/z 50 that is too low to meet 524.2 and 8260 criteria and an abundance of m/z 174 that may be too high, even for CLP-SOW tuning.
2. After completing the Autotune procedure, choose Edit MS Params (under the AdjParam menu item) which will display the screen shown in Figure 7.

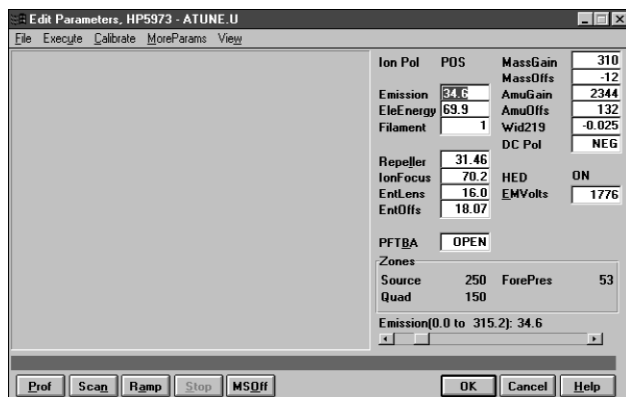


Figure 7. The Edit Parameters screen found by selecting AdjParam/Edit MS Params in the main Manual Tune window.

3. Two changes are required in the default values used for adjusting parameters in this view. First, under the MoreParams menu, choose Ramp Params and change the “Stop” value for the ion focus to 140 as shown in Figure 8. Close this window and choose

AcqParams under the MoreParams window and change Mass 3 from 502 to ion 50 as shown in Figure 9. Close this window and return to the main Edit Parameters screen (Figure 7).

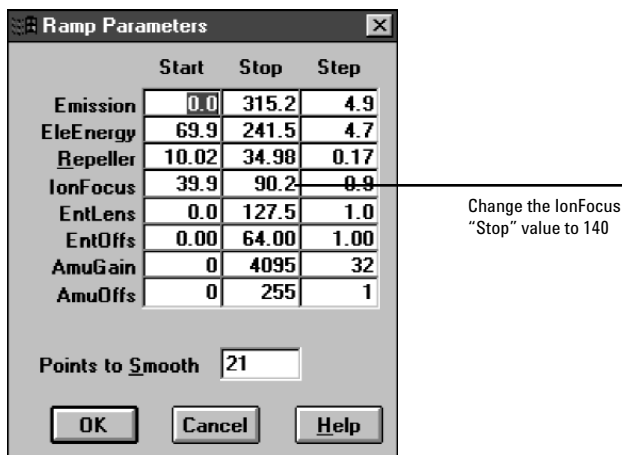


Figure 8. This window allows the user to set ranges for the various tuning parameters. The default ion focus “Stop” setpoint of 90 was set to 140.

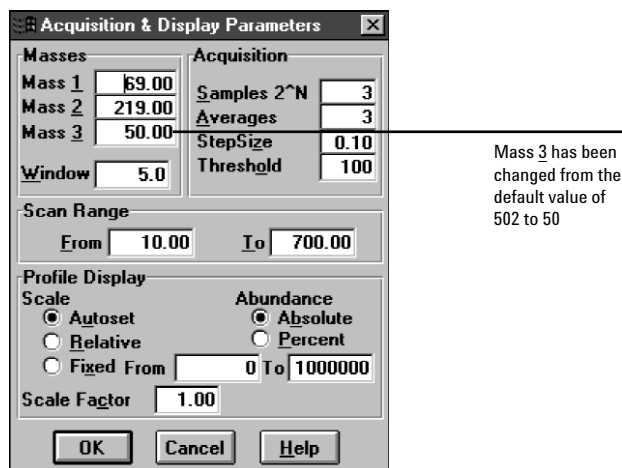


Figure 9. Acquisition and Display Parameters window. M/z values of 69, 219, and 50 have been chosen so that these responses can be ramped and their relative abundances displayed.

4. Highlight the IonFocus window with the cursor and then select Ramp. This gradually ramps the ion focus voltage over the specified range while monitoring the response of ions 69, 219, and 50. After about a minute, a plot of these ion responses vs. the ion focus voltage appears in the window (Figure 10).

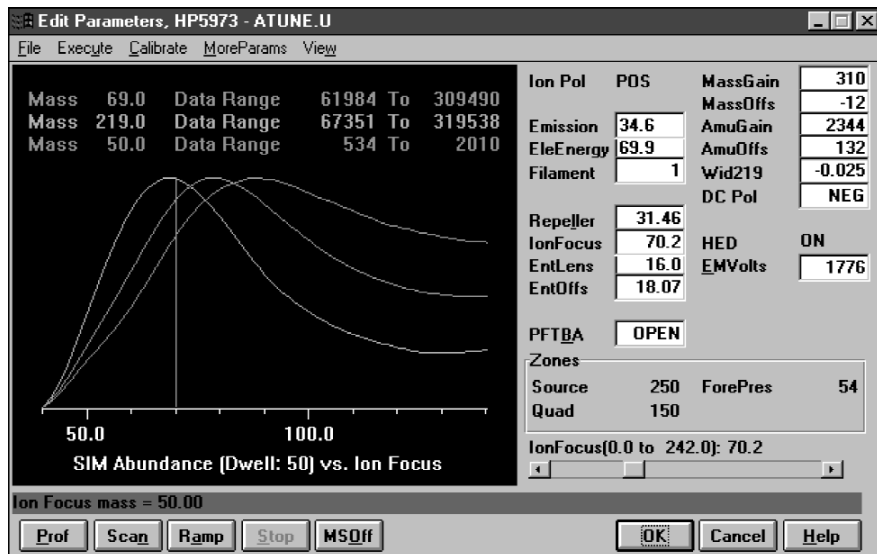


Figure 10. Abundances for ions 69, 219, and 50 while ramping the Ion Focus from 40 to 140.

- Under the View dropdown menu item, choose Expand. This view shows the current Ion Focus setting, the abundance of m/z 69 and the relative abundances of ions 219 and 50 (Figure 11). From the plot, it is easy to see that an increase in the Ion Focus value should increase the 50:69 ratio while reducing the 219:69 ratio. These are

exactly the changes that should enable the MSD to pass BFB tuning criteria.

Note that the ion focus ramping procedure can also be performed from the main Manual Tune screen by choosing Ramp/Ramp Ion Focus on the dropdown menu.

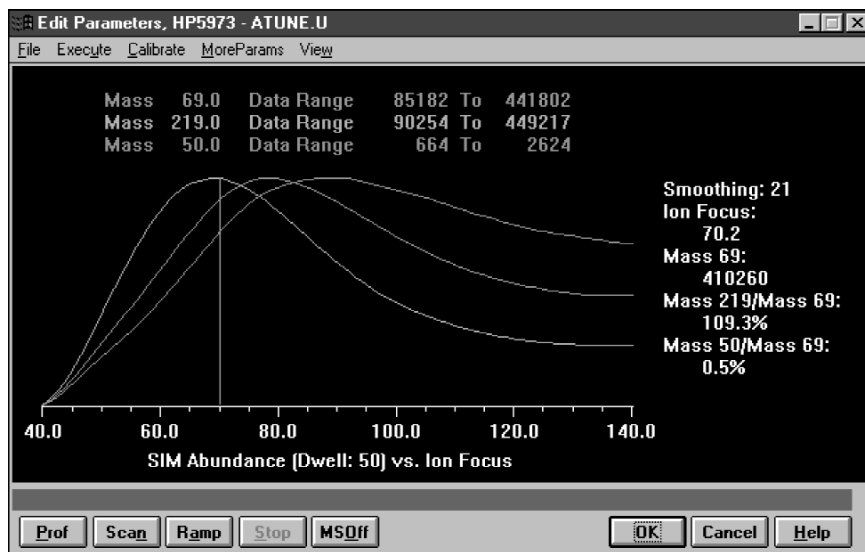


Figure 11. An expanded view of the SIM-Abundance-vs-Ion Focus plot obtained by selecting View/Expand. This view allows one to drag the vertical line to different setpoints while observing changes in the ion relative abundances.

- The vertical line indicates the current ion focus setpoint. Use the cursor to drag this setpoint line to the right while observing the change in the 219:69 and 50:69 ratios. Agilent laboratories have had good success by setting the Ion Focus to values between 100 and 135 V. This should result in a 219:69 ratio in the 60-80% range and a 50:69 ratio that is 0.8 or greater. If tuning to meet 524.2 requirements, the 219/69 ratio should be on the low side of this range.
- Click OK and return to the Manual Tune screen. Under the Calibrate menu item, choose Adjust Abundances, which will automatically reset the electron multiplier to get ion abundances in the optimum range. Save the tune, choosing a new name for the tune file (for example, BFB1.U). Return to Instrument Control (View/Instrument Control) and be sure to select this tune file for the method used to acquire the BFB checkout chromatogram. Inject or purge an appropriate amount of BFB and evaluate the tune using the software tools provided (Figures 2 through 4). Assuming that it passes, assign this tune to the P&T/GC/MS volatiles method in use.

An alternative to the above procedure is to select Scan in the Edit Parameters window (Figure 7) while monitoring ions 69, 219, and 50. The 219:69 and 50:69 ratios are displayed under the Relative Abundance heading and are updated with each scan. Highlight the Ion Focus setting and adjust its value using the slider bar. The effect of different Ion Focus values will be seen almost immediately in the ion ratios. These ratios will bounce around somewhat, but trends can be seen over a few scans. A good choice for the 50:69 ratio would be about 0.85.

Figure 12 shows the spectrum (average of the three scans across the apex with baseline subtraction) for a 1- μ L syringe injection (50 ng/ μ L split 50:1) of BFB using an ion focus value of 115 V. All other parameters (except for the electron multiplier) were set by the Autotune algorithm. This spectrum passes any of the tuning criteria listed in Table 1 but has a higher 174/95 ratio than was achieved using the standard BFB tune.

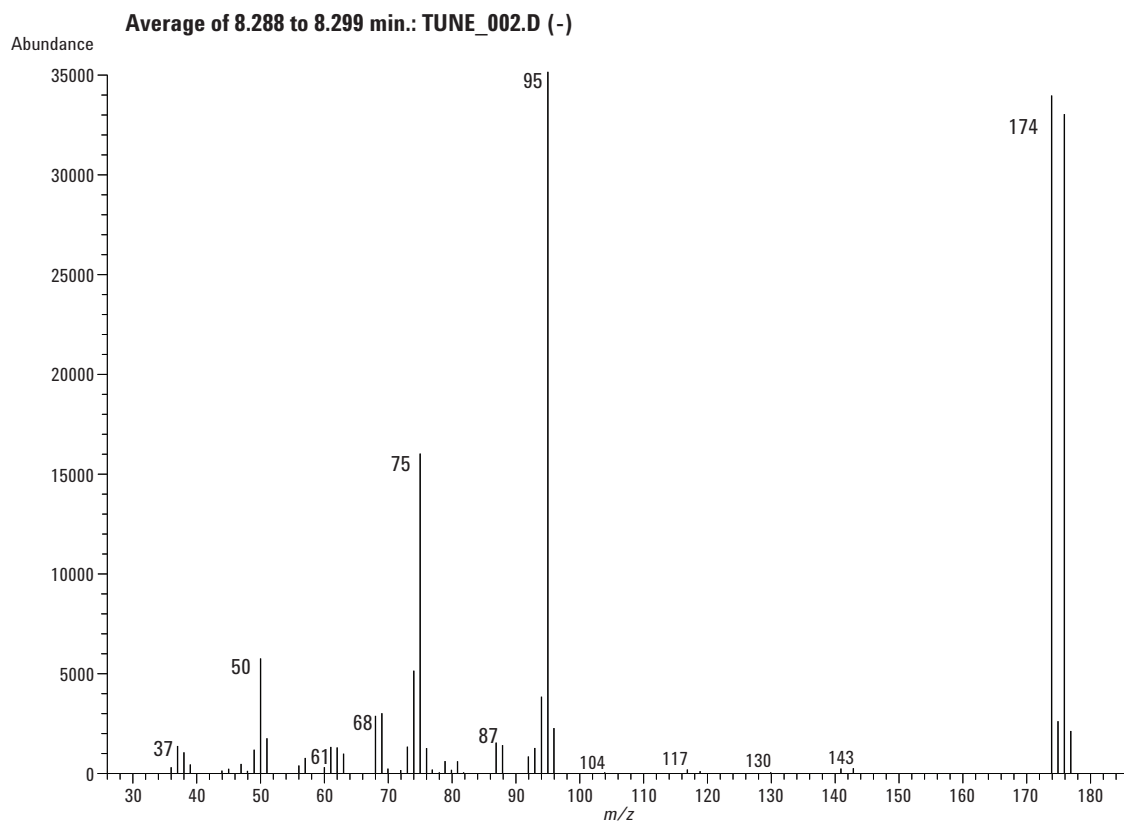


Figure 12. Average spectrum of BFB obtained after using the procedure described under Modified Autotune. After running a standard Autotune, the Ion Focus value was increased to 115 V.

The true test of a successful BFB tune is whether it holds up during repetitive VOC analyses and through normal instrument maintenance procedures. In one extreme test, the same BFB tune easily passed CLP-SOW criteria during a period when two different MSD sources were installed and four different filaments were used. On one Agilent 6890/5973 GC/MS instrument this procedure did not work until the MSD source was cleaned.

Finally, a note of caution is appropriate. While these techniques have worked well for the Agilent 6890/5973A and N GC/MSD systems, this does not imply that the same procedures are appropriate for older Agilent MSDs. Tuning frequency is dictated by the nature of the samples, choice of column and other factors such as column bleed and source cleanliness. If the source becomes too dirty, it must be cleaned in order to pass BFB tuning criteria, no matter which approach is taken.

Modified Autotune Summary

These steps summarize the procedure for modifying the standard Agilent 5973 Autotune to pass BFB tuning criteria. It is provided here as a quick reference guide for those who are already familiar with tuning procedures.

1. In the Manual Tune portion of the Agilent GC/MS ChemStation software, perform a standard Autotune.
2. In the Ramp Parameters window, change the Ion Focus Stop value to 140.
3. In the Acquisition & Display Parameters window, change ion 502 to 50.
4. In the Edit Parameters window click on Ion Focus and then on Ramp.
5. Adjust the Ion Focus value so that the 50/69 ratio is 0.8 or larger. The 219/69 ratio usually falls in the 60 to 80% range. When this PFTBA ion ratio is under 70%, the 174/95 ratio of BFB is usually under 100%.
6. In the Manual Tune window under the Calibrate menu item, adjust ion abundances.
7. Save the tune file with a new name, assign it to the method and verify that the tune passes by injecting a BFB sample according to the method requirements.

Conclusions

There are several ways to tune the Agilent 6890/5973 GC/MSD system to meet any of the USEPA BFB tuning criteria. However, factors such as source cleanliness, choice of column, flow rates and instrument-to-instrument variability make each GC/MSD system unique. Automated BFB and target tuning procedures are normally successful but the 174/95-ion ratio may not be high enough to meet laboratory needs. In our experience, the most robust and long-lasting BFB tunes were generated by the procedure outlined above under Modified Autotune. The procedure takes just a few minutes to complete.

References

1. *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*, Method 524.2, revision 4.1, U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Cincinnati, OH (1995).
2. *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*, Method 8260B, revision 2 (1996).
3. *USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM04.2*, USEPA Contract Laboratory Program, Office of Emergency and Remedial Response.

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