Agilent

Agilent 5977 Series MSD System

Concepts Guide

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This guide applies to the Agilent Mass- Hunter Software -- Data Acquisition for 5977 Series MSD program version B.07.00 or higher until superseded.

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In This Guide...

The Concepts Guide explains the operation of the Agilent 5977 Series MSD by helping you understand how the hardware and software work.

1 Overview

Learn how the Agilent 5977 Series MSD helps you do your job.

2 MSD Theory and System Components

Learn the concepts you need to understand how the Agilent 5977 Series MSD works.

3 MassHunter Acquisition Software

Learn how the Agilent MassHunter Data Acquisition Software controls the Agilent 5977 Series MSD.

4 Chemical Ionization Theory

Learn the theory behind Chemical Ionization in GC/MS.

Contents

1 Overview

This chapter provides an overview of the Agilent 5977 Series MSD system components and how they work together to acquire data and analyze results.

System Description

The Agilent 5977 Series MSD is a stand-alone capillary GC detector for use with Agilent gas chromatographs. The Agilent 5977 Series MSD features:

- Local control panel (LCP) for locally monitoring and operating the MSD
- One of two different high vacuum pumps
- One of three different foreline pumps
- Four different types of independently MSD heated electron-ionization (EI) sources available: standard (stainless), inert, extraction (XTR), and high efficiency (HES)
- Optional chemical ionization (PCI/NCI) modes are available that add a chemical-ionization (CI) source, reagent gas flow controller and plumbing, and CI tuning calibration
- Independently MSD-heated hyperbolic quadrupole mass filter
- High-energy dynode (HED) electron multiplier detector
- Independently GC-heated GC/MSD interface

This configuration has advantages for many applications. The data is acquired through the use of the Agilent MassHunter Data Acquisition software. MassHunter Qualitative and Quantitative Analysis software packages are provided for analyzing the acquired data.

5977 Series MSD applications

The Agilent 5977 Series MSD system provides low detection limits in complex matrices, as well as high temperature, inert ion source options. This supports many analytical applications for active compounds and late-eluters, including pesticides, endocrine disruptors, and hazardous chemicals.

Data acquisition

The MassHunter Data Acquisition software allows you to perform the following tasks from a single window.

Prepare the instrument

- Start and stop the instruments from the software
- Download settings to the GC and the MSD in real time to control the instrument
- Optimize MSD parameters automatically or manually through Agilent tuning programs and print an Autotune report
- Monitor the actual conditions of the instrument
- View the real-time plot for chromatograms and instrument parameters (both GC and MSD) and print a real-time plot report
- View the centroid line spectrum of a peak or the mass range profile spectrum of a peak in real time

Set up acquisition methods

- Enter and save parameter values for the GC and the MSD to an acquisition method
- Select and label the total ion chromatograms or extracted ion chromatograms that you want to appear in the real-time plot
- Set up time segments for each scan type and analysis where parameters change with the time segment or with the scans within the time segment
- Set up SIM/Scan methods using the MassHunter Method Editor
- Print an acquisition method report

Acquire data

- Enter sample information, pre- or post-programs (scripts), and run single sample
- Enter and automatically run both individual samples and samples organized in a sequence
- Set up pre- and post-scripts to run between samples in a sequence
- Set up and run a sequence to optimize MSD acquisition parameters
- Print a sequence report
- View system events, including start and stop times, run events, and errors
- Print an event log report

To learn how to get started with the Agilent 5977 Series MSD, see the *Agilent 5977 Series MSD Quick Start Guide*.

To learn more about how to use the Agilent 5977 Series MSD with real samples and data, see the *Agilent 5977 Series MSD Familiarization Guide*.

To learn how to do individual tasks with the MSD, see the online help.

To learn more about the Agilent 8890, 9000, and 7890 GCs, see the system documentation supplied with the GC.

Data analysis

MassHunter Quantitative Analysis program

Agilent has designed the quantitative analysis program to help quantify very low amounts of material. The program has the following unique features:

- Imports information directly from the acquisition method
- Provides a curve-fit assistant to test all fits and statistics on curve quality
- Presents a batch results window to help you review and operate on an entire batch of data at once
- Automatically detects outliers
- Provides preconfigured templates for basic reporting and provides the capability to create custom reports in Microsoft Excel

Please refer to the *Agilent MassHunter Software – Quantitative Analysis Familiarization Guide* or the online Help for the quantitative analysis program.

MassHunter Qualitative Analysis program

For fast method development, use this software to quickly review the qualitative aspects of the data.

Agilent designed the qualitative analysis program to present large amounts of data for review in one central location. With the program, you can do these operations for any type of mass spectrometer data that you open:

- Extract chromatograms
- View and extract peak spectra
- Subtract background
- Integrate the chromatogram
- Find compounds

You can also set up methods to automatically do the tasks in the list, as well as others, when you open the data files.

Refer to the *Agilent MassHunter Software – Qualitative Analysis Familiarization* Guide or the online Help for the qualitative analysis program.

2 MSD Theory and System Components

This chapter explains how the MSD filters out all but specified ions from reaching the detector before examining the components that make up the Agilent 5977 Series MSD.

Single Quadrupole MSD Operation

This section reviews the theory behind the single quadrupole mass selective detector (MSD).

How a single quadrupole mass selective detector works

A conceptual model can be used to explain the theory of a single quadrupole MSD. See **Figure 1**.

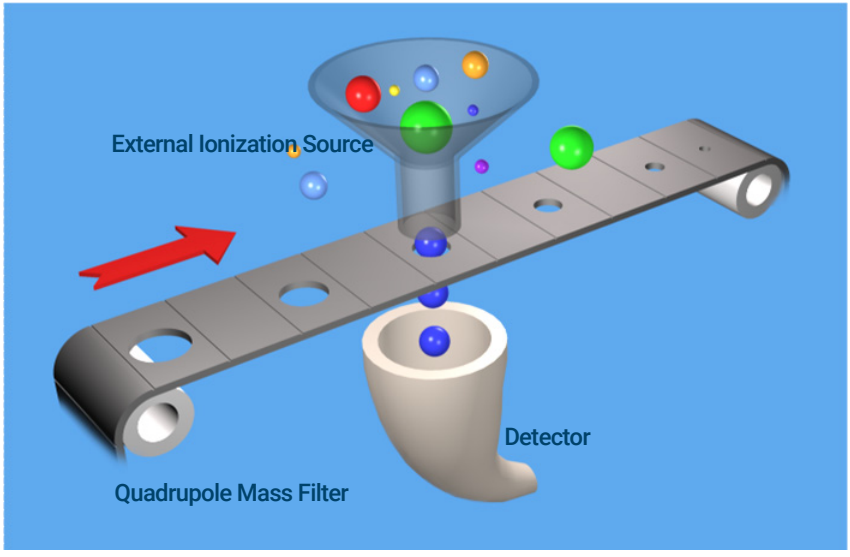

Figure 1. Conceptual model of a single quadrupole MSD

In the model:

- All of the ions contained in a sample are formed in the external ionization source and collected in a funnel. The balls of different colors and sizes represent different ions having different *m/z* values.
- The quadrupole mass analyzer is represented by a moving belt that serves to filter the ions as they pass through openings of various sizes. The ions pass from the funnel, through the filter, to the detector.
- The detector is represented by the collecting funnel below the filtering belt.

As the belt (the analyzer) moves, or the quadrupole settings are changed, ions with different *m/z* values are filtered through the quadrupole.

As the MSD moves from a acquiring data for a small *m/z* value to increasingly larger values, a full scan is created. For a scan acquisition the scan range (for example, *m/z* 50 to 550) is selected by the user. The quadrupole settings are adjusted to filter a single mass for a user specified sampling rate before changing the quadrupole settings for the next ion.

If the belt does not move, the detector continues to monitor a specified *m/z* value over the entire scan period. This type of analysis is known as selected ion monitoring (SIM). The user may set the dwell time in a SIM acquisition for a specific *m/z*. It is the most sensitive operating mode for a single quadrupole mass spectrometer.

SIM acquisition mode

To obtain the best sensitivity for quantitative measurement, the single quadrupole is operated in SIM acquisition mode (**Figure 2**). The duty cycle is the measure of the instrument's time actually devoted to acquiring data. In SIM mode, the quadrupole acquires data for specific ions almost all of the time. This results in nearly 100 % acquisition during the cycle.

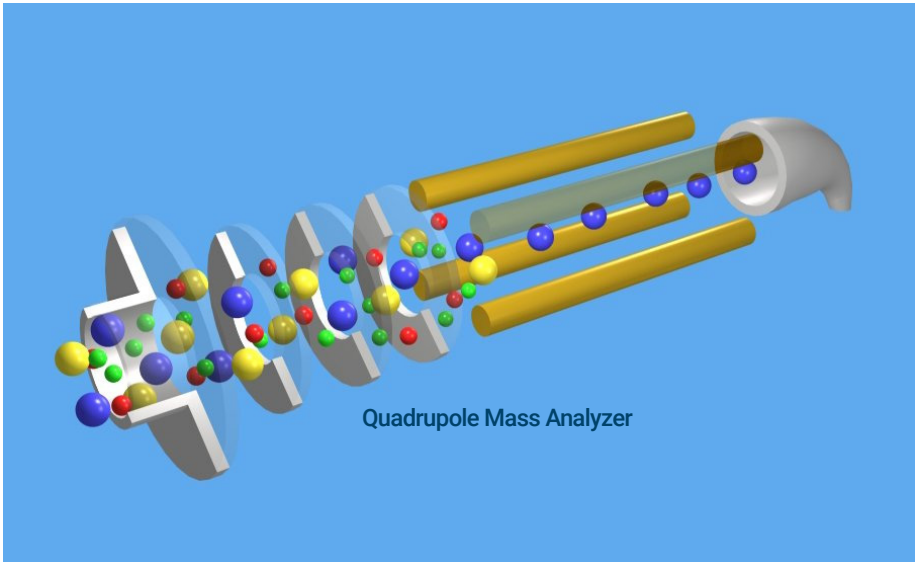

Figure 2. Quadrupole in SIM acquisition mode

In this example:

1 All of the ions (+, –, and neutrals) are formed in the electron impact ionization source.

2 Ion optics guide the ions to the quadrupole mass analyzer.

3 The Agilent electron impact ion source consists of a series of lenses and a repeller assembly that directs the ion beam into the analyzer.

4 In the analyzer, only ions of a particular *m/z* value, represented by blue balls, are allowed to pass through to the detector.

5 The detector completes the analysis.

This system has several advantages:

- Provides the best sensitivity for quantitation
- Increases selectivity
- Improves chromatographic specificity

Scan acquisition mode

In scan acquisition mode, the quadrupole serves as a mass filter over time, and a scan is carried out by stepping through increasing DC and RF voltages. This provides filtering through the corresponding *m/z* values across a mass spectrum. See **Figure 3** on page 17.

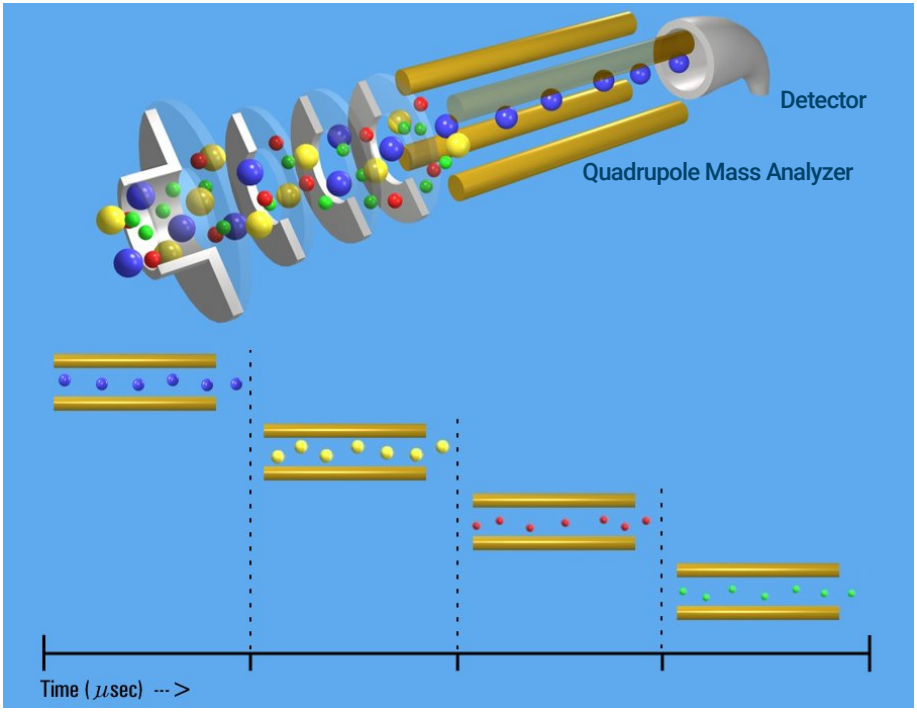

Figure 3. Quadrupole in Scan acquisition mode

The scan acquisition mode is less sensitive because the detection cycle of each *m/z* value is considerably less than 100 %. The quadrupole mass analyzer scans sequentially, passing each *m/z* value in the selected mass range to the detector.

A full scan MS is still a useful mode of operation because it shows all of the ions that are being formed in the ion source giving valuable structural compound information. This structural information is required for developing highly sensitive SIM acquisitions for quantitative analysis.

Mass Spectrometer Components

The main components of a mass spectrometer are the vacuum system, the analyzer, and the electronics.

Vacuum system

The vacuum system creates the high vacuum required for an MSD to operate. Without the vacuum, the molecular mean free path would be very short, and the ions would collide with air molecules, causing fragmentation, before they could reach the detector. In addition, operation at high temperatures would damage analyzer components.

The Agilent 5977 Series MSD uses two vacuum pumps to obtain the necessary vacuum levels. A foreline pump creates a low vacuum, then a high vacuum pump engages to create the type of high vacuum needed for efficient operation. The Agilent 5977 Series MSD can use three different types of low vacuum pumps, and two types of high vacuum pumps.

The parts of the vacuum system are:

- Foreline (rough) pump
- High vacuum (diffusion or turbo) pump
- Side plate (analyzer door)
- Front and rear end plates
- Vacuum seals
- Calibration valve and vent valve
- Vacuum control electronics
- Vacuum gauges and gauge control electronics

The analyzer chamber is the area of the MSD where the analyzer operates. The chamber manifold is extruded from aluminum alloy. Large openings in the side, front, and rear of the chamber are covered by plates, sealing the chamber and keeping the pressure constant. O-rings provide seals between the plates and the manifold openings.

The foreline pump initially reduces the pressure in the analyzer chamber so that the high vacuum pump can operate. It also pumps away the gas load from the high vacuum pump.

The Agilent 5977 Series MSD provides two options for the high vacuum pump: a diffusion pump or a turbo pump system. The diffusion pump supports a maximum recommended flow rate into the MSD of 1.5 mL/min. The diffusion pump uses baffling to prevent vapor from migrating into analyzer chamber. The diffusion pump foreline pressure is monitored by a vacuum gauge, and the diffusion pump heater is controlled by the AC board. Turbo pumps have a screen to keep debris out of the vacuum chamber, but a baffle is unnecessary. There is no foreline gauge for the turbo pumps; the vacuum pressure is controlled by the turbo controller.

Analyzer

The analyzer is the main component of the MSD. In EI mode, the sample is vaporized in the GC inlet, separated by compound properties in the GC column, and passes through the GC/MSD interface into the ion source chamber, where it is bombarded with a beam of electrons that have enough energy to ionize and fragment the compound.

The resulting ions are repelled from the ion source into the mass filter. The mass filter allows ions of a selected mass-to-charge ratio to pass through the filter and strike the detector. The detector generates a signal current proportional to the number of ions striking it.

The analyzer is attached to the vacuum side of the side plate. The side plate is hinged for easy access. The ion source and mass filter are heated independently. Each is mounted inside a radiator for correct heat distribution.

The main components of the analyzer are:

- Ion source
- Mass filter
- Detector
- Heaters and radiators

The ionization of a sample occurs in the ion source that is shown, schematically, on the left in **Figure 4**. In this case, the source used is an electron ionization (EI) source, which ionizes the sample with a charged filament.

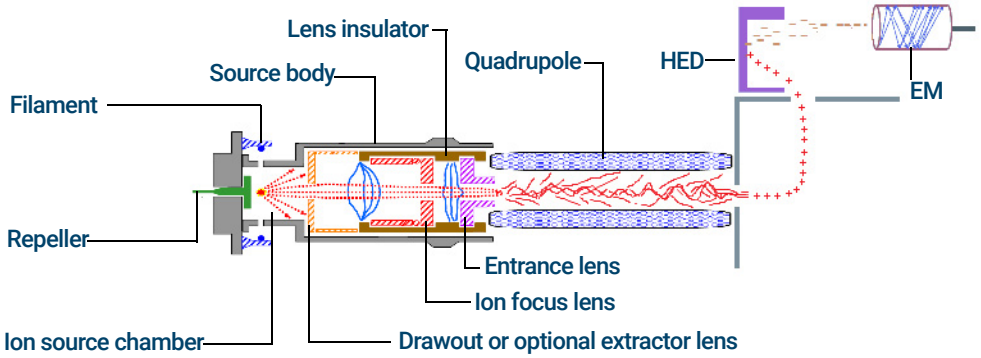

Figure 4. MSD analyzer components

Ion source

The EI source operates by electron ionization. The sample enters the ion source from the GC/MSD interface. Electrons emitted by a filament enter the ionization chamber, guided by a magnetic field. The high energy electrons interact with the sample molecules, ionizing and fragmenting them. The positive voltage on the repeller pushes the positive ions into the lens stack, where they pass through several electrostatic lenses. These lenses concentrate the ions into a tight beam, which is directed into the mass filter.

Figure 5 on page 21 shows an exploded view of an EI source. There are two types of lens stacks for the EI sources available for the Agilent 5977 Series MSD. The source type pictured uses a nonadjustable static drawout plate lens, and adjustable ion focus and entrance lenses. The other type of lens stack available replaces the static drawout lens with an adjustable voltage extractor lens for improved sensitivity.

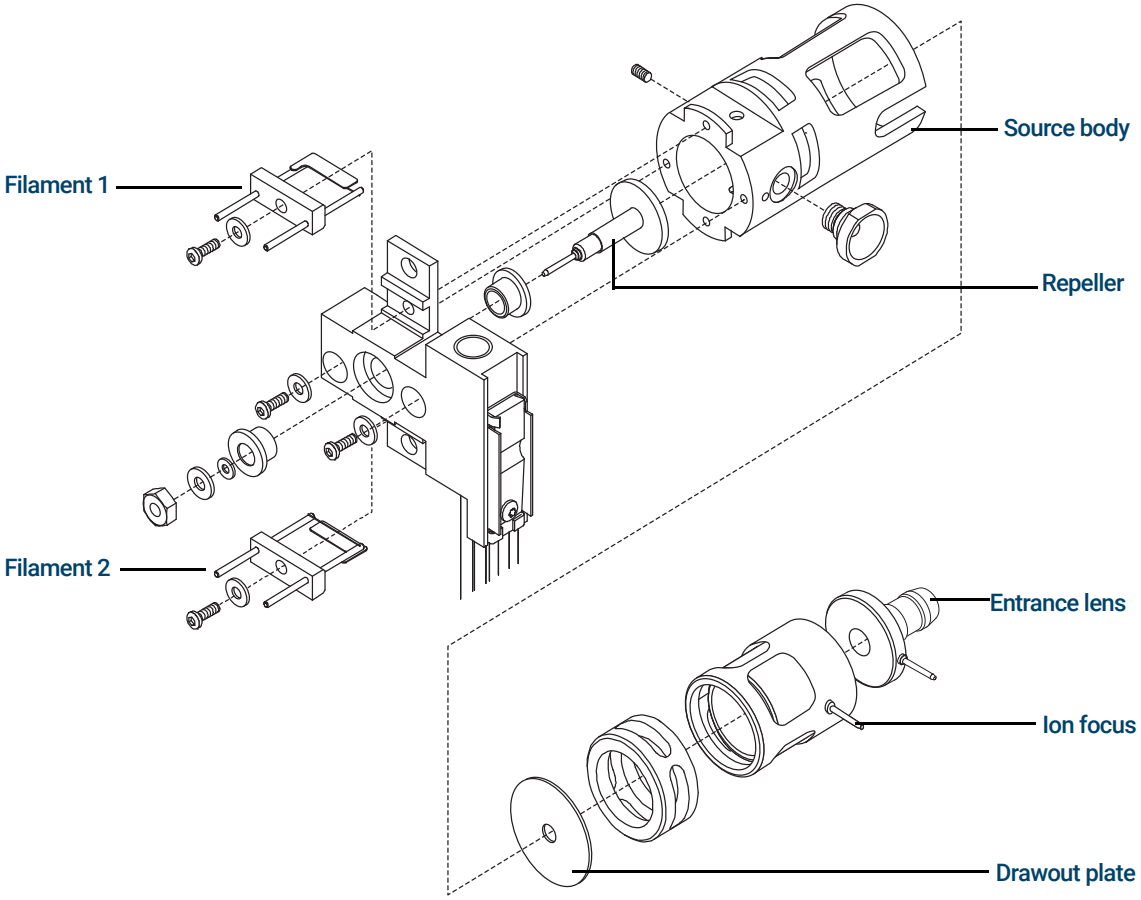

Figure 5. EI source with static drawout lens

The ion source body is a cylinder that holds the other parts of the ion source, including the lens stack. With the repeller and lens stack making up its front and back walls, the ionization chamber is the space in the source body where the ions are formed. Slots outside the ionization chamber in the source body help the vacuum system to pump away carrier gas any unionized sample molecules or fragments.

A CI source is similar to the EI source, but only has one part in common with the EI source - the entrance lens. A CI source only has one filament, as opposed to an EI source which has two. The single CI filament has a straight wire and a reflector. A dummy filament provides connections for the other wires.

The unsealed holes in the CI source (electron-entrance and ion-exit) are very small (0.5 mm), making it possible to pressurize the ionization chamber. Both the source body and the plate are at repeller potential, electrically isolated from the radiator and the CI interface tip. The seal for the interface tip ensures a leak-tight seal and electrical isolation between the CI interface and the source.

Filaments

The filaments are the key components of the ion source. Two filaments are located on opposite sides of the outside of an EI source. One filament is active at a time. The active filament carries an adjustable AC emission current. The emission current heats the filament causing it to emit electrons, which ionize the sample molecules. In addition, both filaments have an adjustable DC bias voltage. The bias voltage determines the energy on the electrons, usually -70 eV.

The CI source has only one filament of a different design from the EI filaments. A "dummy" filament provides connections for the Filament 2 wires.

When running the instrument in EI mode, you can select which filament in the ion source is active since sometimes one source gives better results than the other. In the CI source, it is always Filament 1.

Magnet

The field created by the magnet directs the electrons emitted by the filament into and across the ionization chamber. The magnet assembly is a permanent magnet with a charge of 350 gauss in the center of the field.

Repeller

The repeller forms one wall of the ionization chamber. A positive charge on the repeller pushes positively charged ions out of the source through a series of lenses. The repeller voltage is also known as the ion energy, although the ions only receive about 20% of the repeller energy.

Drawout plate

The drawout plate forms the back wall of the ionization chamber in the SST and Inert ion sources. The ion beam passes through a hole in the drawout plate and into the drawout cylinder. The drawout cylinder is slotted. The slots correspond to slots in the source body. These slots allow gas and unionized sample molecules or fragments to be pulled away by the vacuum system. The drawout plate and drawout cylinder are both at ground potential.

Extraction lens

The extraction lens forms the back wall of the ionization chamber in the XTR ion source. The ion beam passes through a hole in the lens and into a slotted cylinder. The slots correspond to slots in the source body. These slots allow gas and un-ionized sample molecules or fragments to be pulled away by the vacuum system. The extraction lens and cylinder are both at ground potential.

Ion focus

Increasing the ion focus voltage improves sensitivity at lower masses. Decreasing the ion focus voltage improves sensitivity at higher masses. Incorrect ion focus adjustment results in poor high mass response.

Entrance lens

The entrance lens is at the entrance to the quadrupole mass filter. This lens minimizes the fringing fields of the quadrupole, which discriminate against high-mass ions. There is a permanent +4.4 V voltage added to the entrance lens. The total voltage applied to the entrance lens is the sum of the entrance lens offset, entrance lens gain, and the +4.4 V permanent offset.

Entrance lens voltage = +4.4 VDC + offset + (gain × mass)

Once through the source, the ions are analyzed by a mass analyzer (mass filter) that controls the motion of the ions as they travel to the detector to be converted into actual signals.

Quadrupole

The AMU gain and offset are quadrupole parameters that permit an ion with a specific *m/z* to travel in a stable path through the quadrupole mass filter. These values are ideally adjusted to obtain unit mass tuning ions having a peak width at half-height of 0.5 AMU.

Detector

The detector in the MSD analyzer is a high energy conversion dynode (HED) coupled to an electron multiplier (EM). the detector is located at the exit end of the quadrupole mass filter. It receives the ions that have passed through the mass filter. The detector generates an electronic signal proportional to the number of ions striking it. The detector has three main components: the detector ion focus, the HED, and the EM horn.

Detector ion focus

The detector ion focus directs the ion beam into the HED, which is located off axis. The voltage on the detector focus lens is fixed at -600 V.

High energy dynode

The HED operates at -10,000 V for EI and PCI, and +10,000 V for NCI. It is located off-axis from the center of the quadrupole mass filter to minimize signals due to photons, hot neutrals, and electrons coming from the ion source. When the ion beam hits the HED, electrons are emitted. These electrons are attracted to the more positive EM horn.

EM horn

The EM horn carries a voltage of up to -3000 V at its opening and 0 V at the other end. The electrons emitted by the HED strike the EM horn and cascade through the horn, liberating more electrons as they go. At the far end of the horn, the current generated by the electrons is carried through a shielded cable outside the analyzer to the signal amplifier board.

The voltage applied to the EM horn determines the gain. The voltage is adjustable from 0 to -3000 VDC. As the EM horn ages, the voltage required increases over time.

Analyzer heaters and radiators

The ion source and mass filter are housed in cylindrical aluminum tubes called radiators. The radiators control the distribution of heat in the analyzer. They also provide electrical shielding for analyzer components. The ion source heater and temperature sensor are mounted in the ion source heater block. The mass filter (quad) heater and temperature sensor are mounted on the mass filter radiator. Analyzer temperatures can be set and monitored from the MassHunter Data Acquisition software.

In selecting the temperatures to use, consider the following:

- Higher temperatures help keep the analyzer clean longer
- Higher ion source temperatures result in more fragmentation and therefore lower high-mass sensitivity

Recommended settings (for EI operation):

- Ion source (**“Source temperature guidelines”** on page 41)
- Quadrupole 150 °C

The GC/MSD interface, ion source, mass filter (quad) heated zones interact. The analyzer heaters may not be able to accurately control temperatures if the setpoint for one zone is much lower than that of an adjacent zone.

3 MassHunter Acquisition Software

Overview

MassHunter Data Acquisition Software controls the 5977 Series MSD and GC from the Instrument Control view, shown in **Figure 6**. From here you are able to:

- Control and monitor the 5977 MSD instrument settings
- See the instrument at work through real-time plots
- Automate the running of multiple samples through the sequence table
- Tune (calibrate) the 5977 MSD
- Set up method acquisition parameters for the GC and the MSD
- Monitor the chromatogram and mass spectra as samples are analyzed
- Set up sequences of samples

This chapter provides details for tuning your 5977 MSD and for creating a data acquisition method using MassHunter. Please refer to your online Help for details on other functions you may perform here.

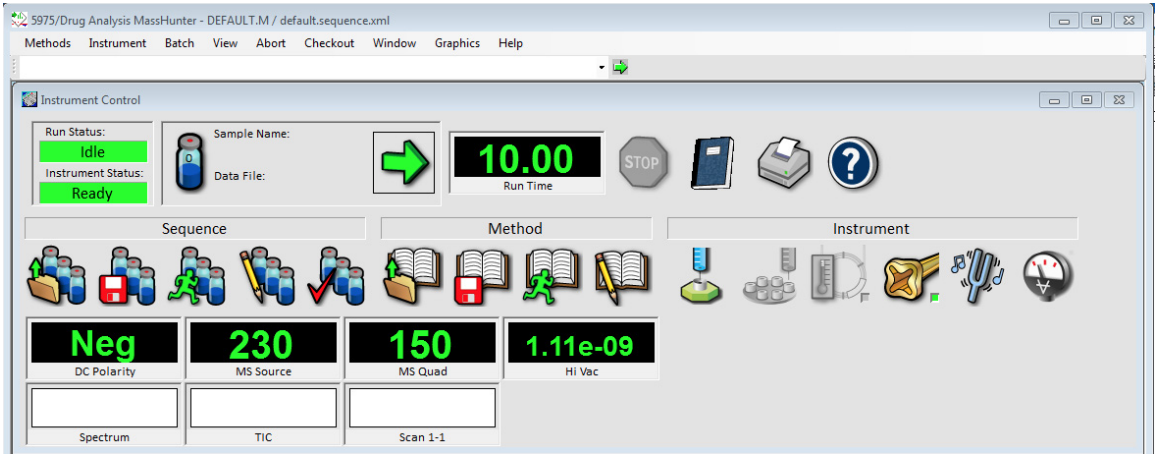

Figure 6. Instrument Control view of the MassHunter Data Acquisition program

General Tuning Concepts

Tuning an MSD involves optimizing a number of instrument parameters such as voltages, currents, and flows. This allows the MSD to achieve the maximum mass spectral sensitivity and proper resolution. The way the instrument is tuned affects all data acquisition. Tuning one parameter often affects the optimum value of other parameters. Some parameters are purely electronic and affect only the way the electronics process the signal. Other parameters affect voltage settings or currents to parts in the MSD's ion source, mass filter, and detector.

Tuning an MS is always performed first in electron ionization (EI) mode, even when preparing to operate in chemical ionization (CI) mode.

The parameters that determine when a compound of a specified mass-to-charge ratio (*m/z*) reaches the detector are optimized during tuning to give the most accurate *m/z* readings of subsequent compounds.

A standard tuning compound located in a vial directly connected to the analyzer chamber is used for tuning an MSD. The tuning compound is introduced into the vacuum manifold when a tune is performed. In the EI mode, perfluorotributylamine (PFTBA) is used for tuning because it is a relatively stable compound. Stability of a tuning compound is important for reproducible tuning. Typically PFTBA lasts one year or longer before replacement is necessary. However, the compound must be volatile enough to flood the ion source so that heating of the tuning vial is unnecessary. The mass spectrum of PFTBA fragments over a wide mass range and is easily interpreted since this compound only has C-13 and N-15 isotopes. During autotune, the fragment compounds 69, 219, and 502 are used for this calibration.

Components adjusted during tuning

During tuning, the ion source element voltages are set to optimize the abundance and ion ratio of each tuning ion fragment reaching the electron multiplier (EM). In addition, the quadrupole AMU gain and offset are set for proper peak width, and the mass axis are set for correct mass assignment. The EM voltage is set to an optimum value and adjusted so that the gain is constant as the EM ages.

To see how this is done in MassHunter, read **"Types of Tuning Available in MassHunter"** on page 35.

Figure 7 shows the MSD and its components with parameters that are adjusted during the tuning process.

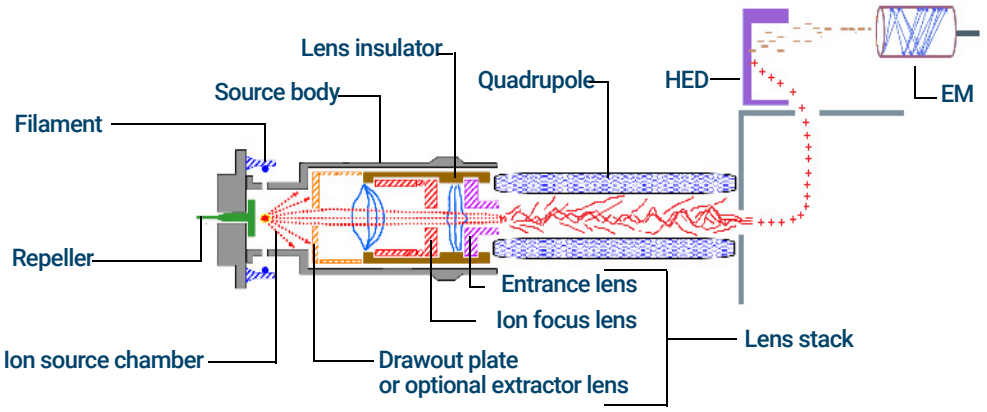

Figure 7. MSD showing components with parameters adjusted during tuning

Filament - The EI source contains two filaments, only one of which is used at any given time. MassHunter allows you to select a filament and set its emission current. One EI filament will usually give better performance than the other. To select the better of the two filaments, run two autotunes, one with each filament, and use the filament that gives the best results. The CI source only has a single filament.

Even though the filament emission current may be set, the default setting is recommended as optimal.

The electron energy, which is the amount of energy on the ionizing electrons, may also be set. However, it is recommended to set the electron energy to 70 eV to produce spectra typically seen with libraries of organic molecules.

Repeller - The repeller accelerates ions out of the ion source chamber toward the lens stack. If the repeller voltage is too low, too few ions leave the source, resulting in poor sensitivity and poor high mass response. If the repeller voltage is too high, too many ions leave the ion source at too high a velocity. This results in fragmentation and the formation of precursor ions, providing poor low-mass response.

Drawout plate - The drawout plate is grounded (not adjustable) acting as a "negative potential". This plate draws cations from the ion source chamber into the lens stack. The drawout plate is one element in the standard, inert, and CI source lens stack.

Extractor lens - This lens is found in the XTR ion source lens stack. It is an adjustable lens with a negative potential that replaces the static grounded drawout lens found in the standard and inert ion sources for improved sensitivity.

Ion focus lens - The ion focus lens is an electrode with a negative potential that works with the other two lenses to "focus" the stream of ions exiting the ion source. Poor ion focus adjustment results in poor high mass response.

Entrance lens - The entrance lens is designed to protrude into the quadrupole entrance to minimize the fringe effects of the quadrupole. Setting the entrance lens voltage in the high end of the allowable range increases the abundances at high mass and decreases the abundance of low mass ions.

Quadrupole - The AMU gain and offset are quadrupole parameters that permit an ion with a specific *m/z* to travel in a stable path through the quadrupole mass filter. These values are ideally adjusted to obtain unit mass tuning ions having a peak width at half-height of 0.5 AMU.

Detector - The High Energy Dynode (HED) operates at -10,000 V and attracts the positively charged ions exiting the quadrupole. The ion beam leaving the quadrupole must turn 90 degrees to reach the HED. This prevents X-rays and photons from influencing the ion count. When the ion beam hits the HED, it creates electrons that are attracted to the less negatively charged EM.

The EM amplifies the signal output by about 10^5. The EM voltage is set to 0-3000 V, and affects sensitivity by increasing the signal output.

Tuning the ion source components

During tuning, the voltage applied to an adjustable ion source component is varied to determine the voltage that gives the maximum abundance for each of the three tuning ions. An example of varying the voltage on the repeller is seen in **Figure 8** on page 30. The voltage selected during an autotune is not usually one of these three peak values. As seen in **Figure 8** on page 30, 24V is optimal for the low tuning mass ion and reduces the abundance of the high tuning mass ion by 50%. Selecting one ions' optimum voltage over the other can change the ion ratios dramatically.

Also, adjusting the voltage of the next component changes the abundance values from the previous component's optimized voltage. This process, by nature, is iterative. Fortunately MassHunter autotune is very good at selecting the component voltages that work best for the ions in this autotune range (*m/z* 69 to 502).

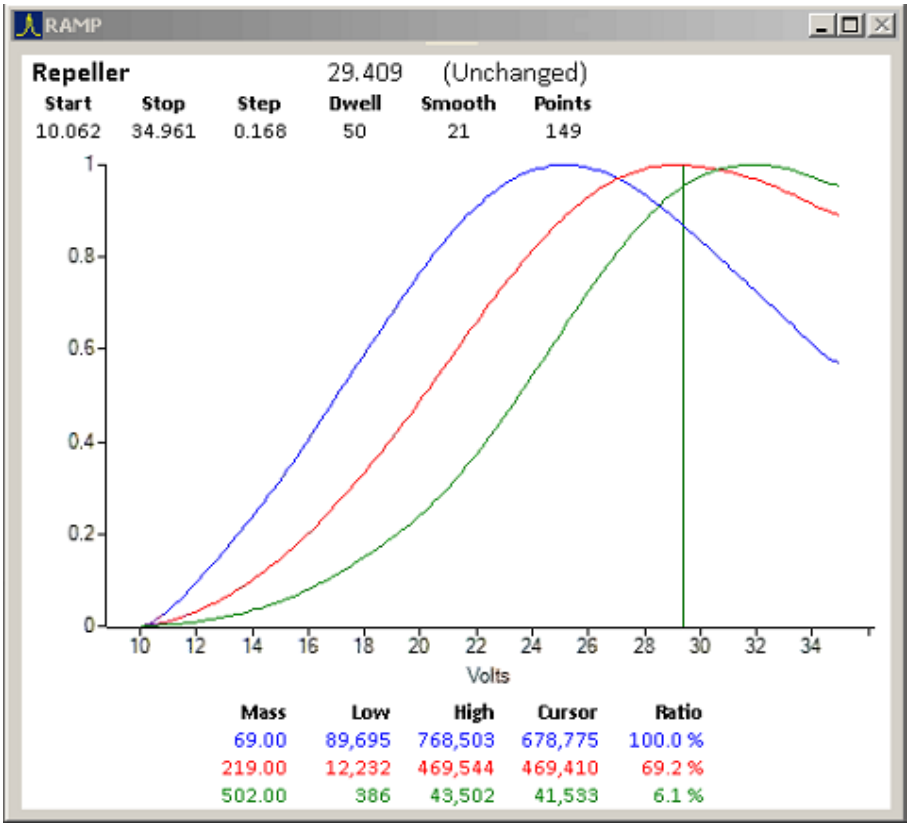

Figure 8. Ramping the repeller voltage to find the value of maximum abundance for the 3 tuning ions

To optimize the voltage readings for a different range of ions, you can start with the autotune results and use manual tuning to refine these parameter while interactively adjusting voltages for different abundances and ion ratios. These targeted values are determined by your application.

Tuning the Quadrupole

The quadrupole mass filter separates ions according to their mass-to-charge ratio (*m/z*). At any given time, only ions of a selected *m/z* can pass through the filter to the detector. The mass filter in the Agilent 5977 Series MSD is a quadrupole.

The quadrupole is a fused-silica (quartz) tube coated with a thin layer of gold. The four hyperbolic surfaces create the complex electric fields necessary for mass selection.

Segments 180 degrees apart are electrically connected. Segments 90 degrees apart are electrically isolated from each other. Radio frequencies of adjoining segments are 180 degrees out of phase with each other. One connected pair has a positive DC voltage added to the RF voltage, the other connected pair has a negative DC voltage added to the RF voltage. The pair with a positive bias is the high pass filter that filters out all masses lower than the selected *m/z*. The pair with a negative bias is the low pass filter that filters out all masses higher than the selected *m/z*.

A varying RF voltage combined with a DC voltage is applied to the two pairs of segments. The magnitude of the RF voltage determines the *m/z* of the ions that pass through the mass filter and reach the detector. The ratio of DC-to-RF voltages determines the resolution (widths of the mass peaks). There are two parameters that control the DC and RF voltages:

- AMU gain
- AMU offset

The quadrupole filters out all ions except those of one or more *m/z* values as determined by the different voltages applied to the pairs of hyperbolic surfaces.

As the voltages are increased, ions with increasing *m/z* values are allowed to pass through. A full MS scan is obtained by increasing the opposite polarity but keeping the same magnitude DC voltage with the same RF voltages applied to the connected pairs of hyperbolic surfaces over an expanded range of values.

AMU mass adjustments

Figure 9 shows a plot of increasing opposite polarity DC voltage and 180 degree out of phase RF voltage applied to the adjacent hyperbolic surfaces of a quadrupole mass filer. This plot is known as a Mathieu Stability Diagram. The shaded area represents a stable region that allows the 152 *m/z* ion to pass through the quadrupole and be counted by the detector. The region to the left of this stable region filters out all ions with a lower *m/z*, the region to the right filters out all ions with a higher *m/z* value. The stable region also includes overlapping stable regions for other ions allowing them to also pass through the quadrupole. To obtain unit resolution on the 152 *m/z* ion the quadrupole must be adjusted so that only ions with an *m/z* of 151.5 to 152.5 can reach the detector.

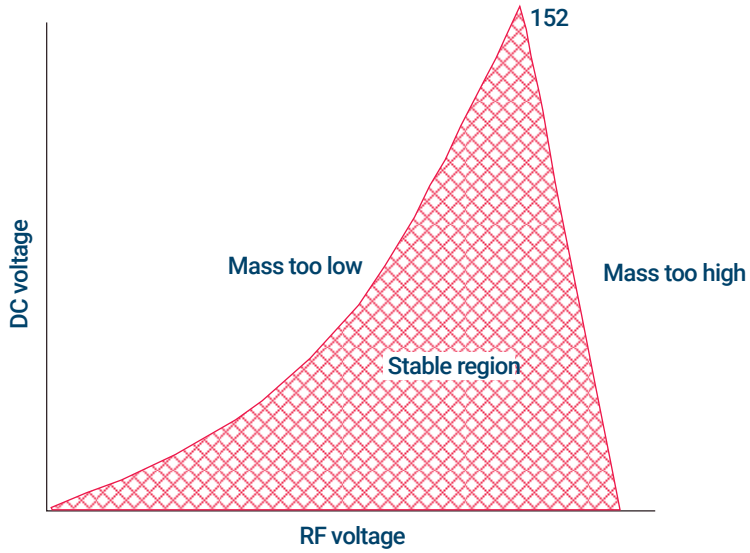

Figure 9. Mathieu Stability Diagram for a single ion

Figure 10 on page 33 is an example of a Mathieu Stability Diagram showing how the detection of 3 ions vary with the DC and RF voltages on opposing poles of the mass filter. Each DC/RF pair that allows a certain mass/charge to oscillate with stability through the quadrupole is indicated by a separate curve. The goal is to obtain a unit mass resolution and a half height peak width of 0.5 AMU by varying the AMU Gain and AMU Offset. The slope of the Scan line is the AMU Gain. Its Y-axis intercept is the AMU Offset. If you examine where the Scan line intersects the stability curves for these three ions in **Figure 10** on page 33 you will see that the region above the Scan line has a unit resolution for these three ions. Increasing the lines offset improves specificity at the cost of resolution and peak width.

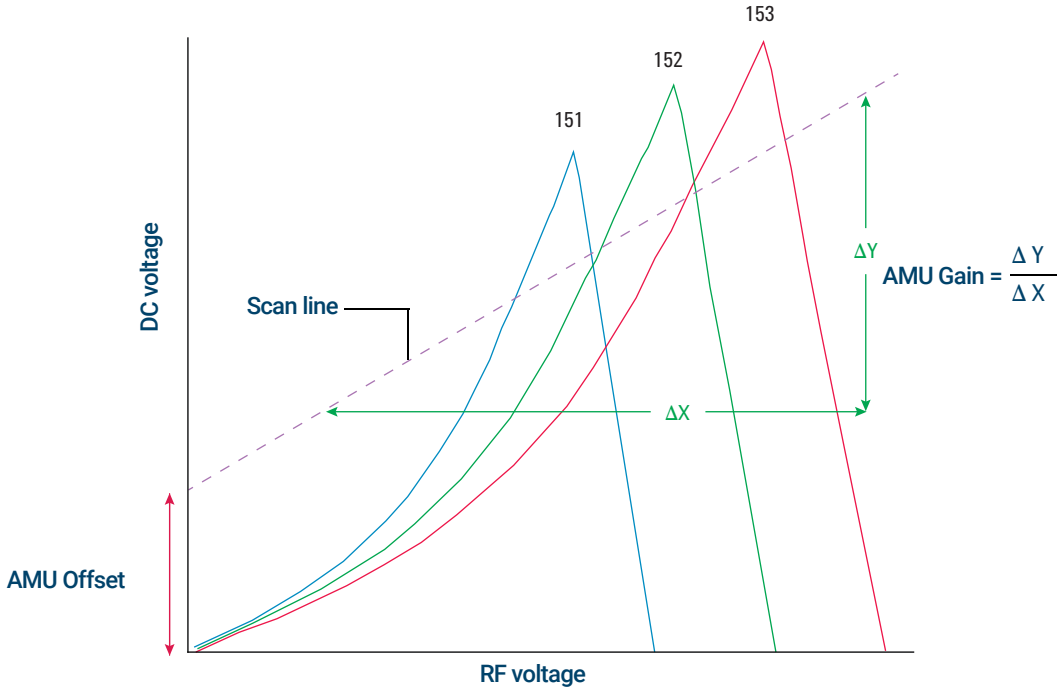

Figure 10. Diagram showing AMU Gain and Offset for 3 ions

The slope of the scan line is the AMU Gain. Adjusting the AMU Gain affects the ratio of DC voltage to RF frequency on the mass filter, which controls the mass of the ions filtered by the mass analyzer and the width of the mass peaks. A higher gain gives narrower peaks. Changing this parameter has a greater effect on the high mass peaks than on the low mass peaks. (See **Figure 11** on page 34.)

Similar to AMU Gain, AMU Offset can also control the widths of the mass peaks. A higher offset also yields narrower peaks equally at all masses. (See **Figure 11** on page 34.) Another part of the tuning process is calibration of the mass axis to within ± 0.2 AMU.

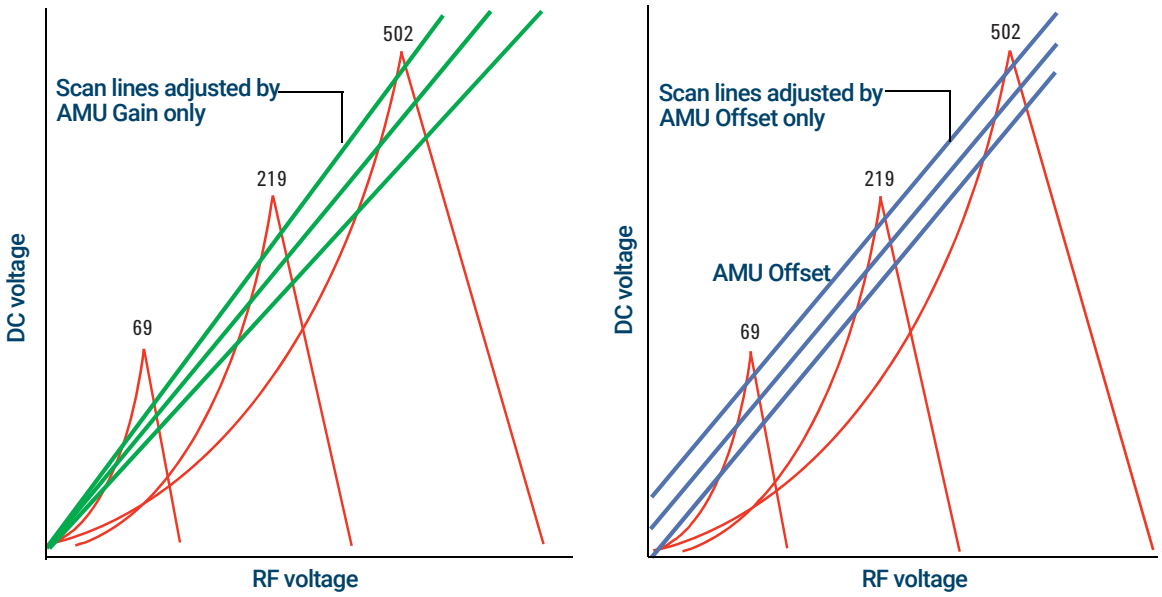

Figure 11. Diagram showing effects of AMU Gain and Offset adjustment for 3 ions

Types of Tuning Available in MassHunter

There are four types of tunes that can be performed with MassHunter:

- Autotune
- Manual tune
- Quick tune
- Target tune

Here we will discuss Autotune and Manual tune. See your online Help for details on Quick tune and Target tune.

Autotune

During an autotune, MassHunter calibrates the instrument to maximize sensitivity across the entire scan range where the three major ion fragments of the tuning compound PFTBA are found. The ions used for tuning are 69, 219, and 502 *m/z*. Autotune is the best choice for those applications that require maximum sensitivity across this entire scan range. To increase maximum sensitivity for a narrower range you can manually tune the instrument.

When the autotune completes, MassHunter generates an autotune report showing settings that the autotune selected for the key analyzer hardware parameters. The tune report lists the optimal settings to use for subsequent analyses, in order to obtain the best sensitivity from your instrument.

Once the lens settings are optimized in the autotune, the EM voltage is adjusted to best capture the ion abundances. The EM voltage amplifies the ion current from the mass filter to meet the target signal abundances. The degree of amplification applied to the EM voltage is described by the EM Gain value. During an autotune a gain curve is used to adjust EM voltage to maintain the same abundance values for the tuning ions as previous autotunes. This adjusts for EM degradation over time requiring higher voltages to keep results between tunes consistent while prolonging EM life.

The EM Gain can be adjusted to produce the signal necessary to analyze very small quantities of compound in the sample, such as trace analyses.

Manual tune

The Manual Tune feature allows you to interactively set individual tune parameters. This provides more flexibility in adjusting the performance of your instrument than an autotune. Manual Tune is especially useful for performing diagnostics on the MSD, especially when there is the need to test the instrument for leaks.

Figure 12 shows some of the parameters that can be interactively set during a manual tune.

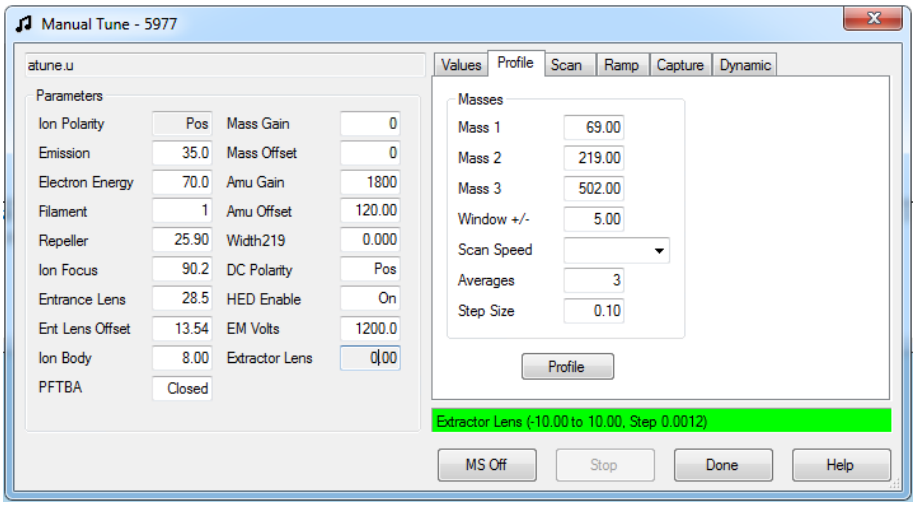

Figure 12. MassHunter Manual Tune dialog

When performing a manual tune, you can alter the lens voltages and examine the effect of this adjustment by executing a profile scan or spectrum scan. A profile scan (SIM) can be performed by entering the required masses for PFTBA (69, 219, 502) in the Profile tab of the Manual Tune screen.

The results of the scan are presented as a real time plot in manual tune. During a manual tune, you can continue adjusting the parameters until the desired effect is achieved.

Mass peak widths can be optimized by adjusting the AMU Gain and AMU Offset settings on the analyzer. For high mass samples, adjusting the AMU Gain has the greatest effect while AMU Offset has an equal effect across the entire mass range.

Mass axis calibration is adjusted by changing the Mass Gain and Mass Offset. Again, for high mass samples, the Mass Gain has the greatest effect on the mass axis, while the Mass Offset adjustments have an equal effect across the entire mass range.

The EM voltage is used to adjust the absolute abundance for all masses, especially *m/z* 69. Adjustments in the Repeller, Ion Focus, Entrance Lens, and Entrance Lens Offset voltages can alter the relative abundance of one mass to another mass.

Finally, after the manual tune is complete, the relationship between EM Gain and EM voltage can be re-established. Once all parameters have been optimized, the required settings can be saved in your own user-created tune file.

MSD Data Acquisition

You create an acquisition method using the MS Method Editor in MassHunter. In addition to GC Run parameters, methods also include MSD data acquisition specifications. There are three types of MSD data acquisition methods available in MassHunter: Scan, Selected Ion Monitoring (SIM), and SIM/Scan.

Scan acquisition type

Select the Scan Acquisition type to scan all the masses within a specific *m/z* range. It is most useful for analyses in which the chemical composition of the sample is unknown. The *m/z* range is specified for the Start Mass and End Mass method parameters shown in the Scan Time Segments table in **Figure 13**. The scan speed parameter for this Time segment is entered in the Scan Speed drop down menu. The higher the scan speed the lower the resolution of the sample data.

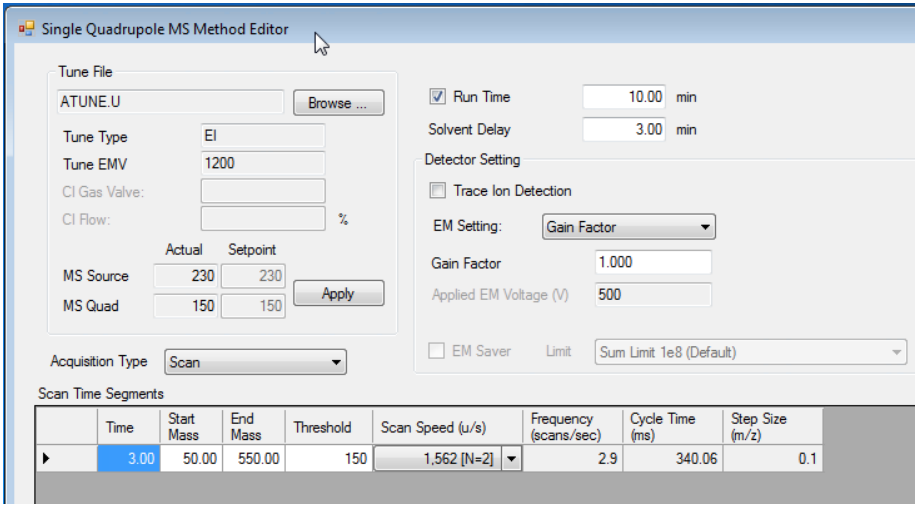

Figure 13. Single Quadrupole MS Method Editor displaying a Scan method

The general acquisition parameters under the operators control are:

- **Solvent delay** - This is the expected time for the elution of the solvent peak from the column. This setting designates the amount of time to wait to turn on the filament voltage. Sending voltage to the filament while the solvent front is eluting can burn out the filament and shorten the life of the electron multiplier.
- **EMV Mode** - This designates if the electron multiplier voltage should be specified as a gain factor, an absolute voltage, or a voltage relative to the tune voltage.
- **MS Source temperature** - See **"Source temperature guidelines"** on page 41.
- **MS Quad temperature**

The scan acquisition parameters under the operators control are:

- **Time** - This is the time at which a Time Segment begins. When a time segment begins, its acquisition parameters becomes active, replacing the previous set of time segment acquisition parameters. The parameters used in a time segment ends when the next time segment begins or at the end of the data acquisition run time.
- **Start Mass** - This is the lowest *m/z* for which data is acquired. The mass range below this setting is not scanned.
- **End Mass** - This is the highest *m/z* for which data is acquired. The mass range above this setting is not scanned.
- **Threshold** -This designates the minimum abundance for a mass abundance pair to be stored as a value included in the spectrum. The lower the threshold, the more mass peaks will be stored.
- **Scan speed** - This is defined by the cycle time and the Mass range. The scan speeds available range from a maximum speed with a sampling rate of 0 to speeds that decline by half as the sampling rate increases by 1. The higher the sampling rate the lower the number a data points on a plotted peak and the higher is the sensitivity.
- **Frequency** - This designates the number of scans/second and is an estimate of the scan speed. A scan speed that gives a frequency reading of 1 scan/second is considered the minimum for good quality data.

- **Cycle Time**- The cycle time is the time required to scan every 0.1 *m/z* typical step size in the ion scan range. It also includes the time to reset the quadrupole to begin the next scan. The time spent to scan each incremental *m/z* value is 40 µs for a sampling rate of 0. A sampling rate of 1 requires a scan time of 80, 2 requires 160 µs, and so on. The mass range multiplied by the steps/*mz,* and sampling time gives us the scan time. The cycle time includes a reset time for the changes in the quadrupole settings to the scan time. A data point for a peak is collected once every cycle.
- **Step Size**- This is the incremental value between scans. The typical value for an MSD is 0.1 *m/z*.

SIM acquisition type

In SIM data acquisition mode, you set the instrument to acquire data for one or more specific *m/z* of interest, as opposed to acquiring data for every ion in a mass range, as is done in the scan mode. SIM mode is used to detect specific compounds with very high sensitivity. This is because in SIM, the instrument is set to collect data on each *m/z* of interest for a time that you specify known as dwell time. The MassHunter Dwell Time parameter is shown on the SIM tab in **Figure 14**. In the SIM tab is also where you can enter one or more specific *m/z* for acquisition. A typical dwell time for SIM mode is 100 msec, which is much longer than a scan. Since the filter is spending a longer time acquiring each specific mass, sensitivity is improved.

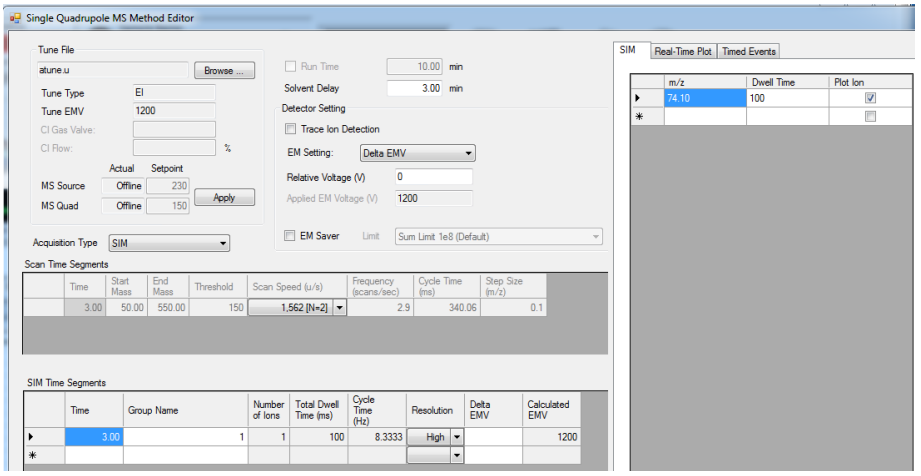

Figure 14. Single Quadrupole MS Method Editor displaying a SIM method

The general acquisition parameters under the operators control are:

- **Solvent delay** - This is the expected time for the elution of the solvent peak from the column. This setting designates the amount of time to wait to turn on the filament voltage. Sending voltage to the filament while the solvent front is eluting can burn out the filament and shorten the life of the electron multiplier.
- **EMV Mode** - This designates if the electron multiplier voltage should be specified as a gain factor, an absolute voltage, or a voltage relative to the tune voltage.
- **MS Source temperature** - See **"Source temperature guidelines"** on page 41.
- **MS Quad temperature**

The SIM acquisition parameters under the operators control are:

- **Time** - This is the time at which a time segment begins. When a time segment begins, its acquisition parameters becomes active, replacing the previous set of time segment acquisition parameters. The parameters used in a time segment ends when the next time segment begins or at the end of the data acquisition run time.
- ***m/z*** - The ion to acquire for the selected time segment.
- **Dwell Time** - The length of time for the detector to count these ions.

SIM and scan acquisition type

This acquisition type lets you specify both Scan Time Segment(s) to acquire all ions contained within a specified mass range while simultaneously acquiring ions of a specific *m/z* value in SIM Time Segment(s). For each time segment entered in a SIM time segment, select the SIM tab located on the right side of the dialog and specify each ion to acquire during that time.

Source temperature guidelines

Below are high level guidelines for setting the source temperate in your GC/MSD. When determining the source temperature consider the effects that this temperature has on chromatographic and chemical stability. Too low a source temperature may cause excessive tailing of higher boiling compounds. Too high a source temperature may cause chemical degradation of fragile compounds.

Suggested source temperatures by application

Do not exceed the maximum temperature limit of the source specified for your instrument.

Forensic & Toxicology: 250-280 °C. Many components (or their derivatives) are adversely affected by high temperatures.

Volatile Compounds: ≈280 °C

Semi-Volatile Compounds: ≈300 °C

PAH and similar: 350 °C: Most compounds are stable at high temperatures and lower temperatures may affect chromatography.

For more information, Agilent application notes provide complete analytical conditions, including MS source and Quadrupole temperatures.

4 Chemical Ionization Theory

Chemical Ionization Overview

Chemical ionization (CI) is a technique for creating ions used in mass spectrometric analyses. There are significant differences between CI and electron ionization (EI). This section describes the most common chemical ionization mechanisms.

In EI, relatively high-energy electrons (70 eV) collide with molecules of the sample to be analyzed. These collisions produce (primarily) positive ions. Upon ionization, the molecules of a given substance fragment in fairly predictable patterns. EI is a direct process; energy is transferred by collision from electrons to the sample molecules.

For CI, in addition to the sample and carrier gas, large amounts of reagent gas are introduced into the ionization chamber. Since there is so much more reagent gas than sample, most of the emitted electrons collide with reagent gas molecules, forming reagent ions. These reagent gas ions react with each other in primary and secondary reaction processes that establish an equilibrium. They also react in various ways with sample molecules to form sample ions. CI formation involves much lower energy and is much more "gentle" than electron ionization. Since CI results in much less fragmentation, CI spectra usually show high abundance of the molecular ion. For this reason, CI is often used to determine the molecular weights of sample compounds.

Methane is the most common CI reagent gas. It yields certain characteristic ionization patterns. Other reagent gases yield different patterns and may result in better sensitivity for some samples. Common alternative reagent gases are isobutane and ammonia. Carbon dioxide is often used in negative CI. Less common reagent gases are carbon dioxide, hydrogen, freon, trimethylsilane, nitric oxide, and methylamine. Different ionization reactions occur with each reagent gas.

WARNING **Ammonia is toxic and corrosive. Use of ammonia requires special maintenance and safety precautions.**

Water contamination in reagent gases decreases CI sensitivity dramatically. A large peak at *m/z* 19 (H_30^+) in positive CI is a diagnostic symptom of water contamination. In high enough concentrations, especially when combined with calibrant, water contamination will result in a heavily contaminated ion source. Water contamination is most common immediately after new reagent gas tubing or reagent gas cylinders are connected. This contamination will often decrease if the reagent gas is allowed to flow for a few hours, purging the system.

References on chemical ionization

A. G. Harrison, *Chemical Ionization Mass Spectrometry*, 2nd Edition, CRC Press, INC. Boca Raton, FL (1992) ISBN 0-8493-4254-6.

W. B. Knighton, L. J. Sears, E. P. Grimsrud, "High Pressure Electron Capture Mass Spectrometry", *Mass Spectrometry Reviews* (1996), 14, 327-343.

E. A. Stemmler, R. A. Hites, *Electron Capture Negative Ion Mass Spectra of Environmental Contaminants and Related Compounds*, VCH Publishers, New York, NY (1988) ISBN 0-89573-708-6.

Positive CI Theory

Positive CI (PCI) occurs with the same analyzer voltage polarities as EI. For PCI, the reagent gas is ionized by collision with emitted electrons. The reagent gas ions react chemically with sample molecules (as proton donors) to form sample ions. PCI ion formation is more "gentle" than electron ionization, producing less fragmentation. This reaction usually yields high abundance of the molecular ion and is, therefore, often used for determining molecular weights of samples.

The most common reagent gas is methane. Methane PCI produces ions with almost any sample molecule. Other reagent gases, such as isobutane or ammonia, are more selective and cause even less fragmentation. Because of the high background from the reagent gas ions, PCI is not especially sensitive and detection limits are generally high.

There are four fundamental ionization processes that take place during PCI at ion source pressures in the 0.8 to 2.0 Torr range. These are:

- Proton transfer
- Hydride abstraction
- Addition
- Charge exchange

Depending on the reagent gas used, one or more of these four processes can be used to explain the ionization products observed in the resulting mass spectra.

EI, methane PCI, and ammonia PCI spectra of methyl stearate are shown in **Figure 15** on page 47. The simple fragmentation pattern, large abundance of the $[MH]^+$ ion, and the presence of the two adduct ions are characteristic of positive chemical ionization using methane as a reagent gas.

The presence of air or water in the system, especially in the presence of PFDTD calibrant, quickly contaminates the ion source.

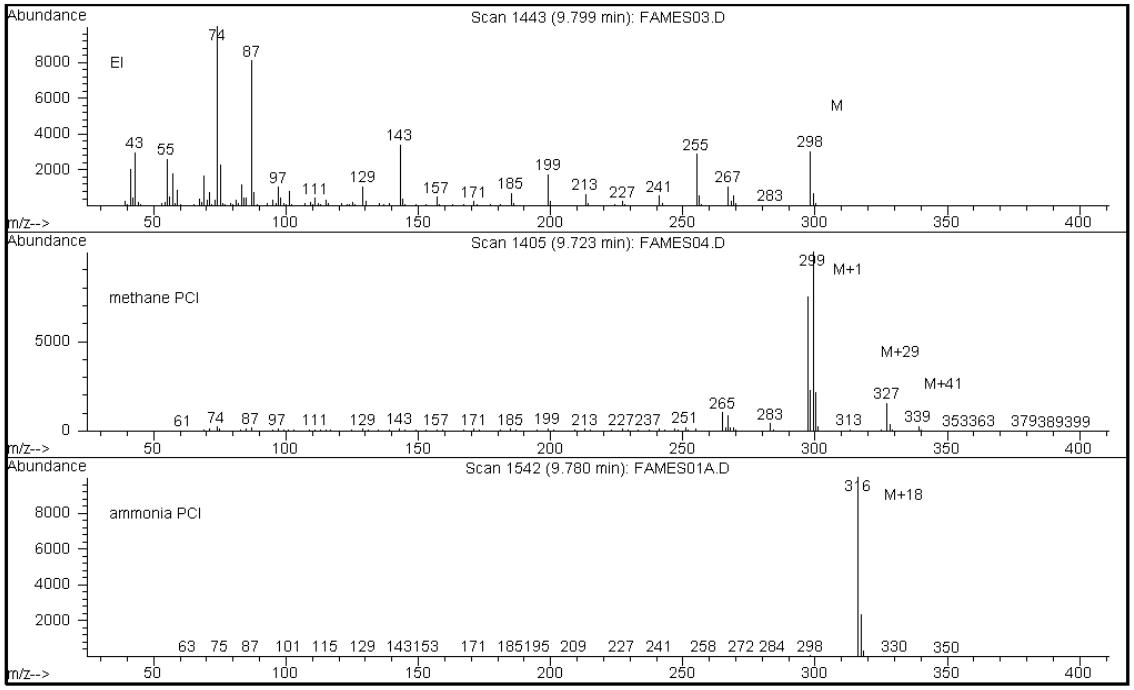

Figure 15. Methyl stearate (MW = 298): EI, methane PCI, and ammonia PCI

Proton transfer

Proton transfer can be expressed as

$$BH^+ + M \rightarrow MH^+ + B$$

where the reagent gas B has undergone ionization resulting in protonation. If the proton affinity of the analyte (sample) M is greater than that of the reagent gas, the protonated reagent gas will transfer its proton to the analyte forming a positive charged analyte ion.

The most frequently used example is the proton transfer from CH_5^+ to the molecular analyte, which results in the protonated molecular ion MH^+.

The relative proton affinities of the reagent gas and the analyte govern the proton transfer reaction. If the analyte has a greater proton affinity than the reagent gas, then proton transfer can take place. Methane (CH_4) is the most common reagent gas because its proton affinity is very low.

Proton affinities can be defined according to the reaction:

$$B + H^+ \rightarrow BH^+$$

where the proton affinities are expressed in kcal/mole. Methane's proton affinity is 127 kcal/mole. Tables **1** and **2** on **page 49** list the proton affinities of several possible reagent gases and of several small organic compounds with various functional groups.

The mass spectrum generated by a proton-transfer reaction depends on several criteria. If the difference in proton affinities is large (as with methane), substantial excess energy may be present in the protonated molecular ion. This can result in subsequent fragmentation. For this reason, isobutane with a proton affinity of 195 kcal/mole may be preferred to methane for some analyses. Ammonia has a proton affinity of 207 kcal/mole, making it less likely to protonate most analytes. Proton-transfer chemical ionization is usually considered to be “soft” ionization, but the degree of the softness depends on the proton affinities of both the analyte and the reagent gas, as well as on other factors, including ion source temperature.

Table 1 Reagent gas proton affinities

Species	Proton affinity kcal/mole	Reactant ion formed
H_2	100	H_3^+ (*m/z* 3)
CH_4	127	CH_5^+ (*m/z* 17)
C_2H_4	160	$C_2H_5^+$ (*m/z* 29)
H_2O	165	H_3O^+ (*m/z* 19)
H_2S	170	H_3S^+ (*m/z* 35)
CH_3OH	182	$CH_3OH_2^+$ (*m/z* 33)
t-C_4H_{10}	195	t-$C_4H_9^+$ (*m/z* 57)
NH_3	207	NH_4^+ (*m/z* 18)

Table 2 Proton affinities of selected organic compounds for PCI

Molecule	Proton affinity (kcal/mole)	Molecule	Proton affinity (kcal/mole)
Acetaldehyde	185	Methyl amine	211
Acetic acid	188	Methyl chloride	165
Acetone	202	Methyl cyanide	186
Benzene	178	Methyl sulfide	185
2-Butanol	197	Methyl cyclopropane	180
Cyclopropane	179	Nitroethane	185
Dimethyl ether	190	Nitromethane	180
Ethane	121	*n*-Propyl acetate	207
Ethyl formate	198	Propylene	179
Formic acid	175	Toluene	187
Hydrobromic acid	140	*trans*-2-Butene	180
Hydrochloric acid	141	Trifluoroacetic acid	167
Isopropyl alcohol	190	Xylene	187
Methanol	182		

Hydride abstraction

In the formation of reagent ions, various reactant ions can be formed that have high hydride-ion (H^-) affinities. If the hydride-ion affinity of a reactant ion is higher than the hydride-ion affinity of the ion formed by the analyte's loss of H^-, the thermodynamics are favorable for this chemical ionization process. Examples include the hydride abstraction of alkanes in methane chemical ionization. In methane CI, both CH_5^+ and $C_2H_5^+$ are capable of hydride abstraction. These species have large hydride-ion affinities, which results in the loss of H^- for long-chain alkanes, according to the general reaction

$$R^+ + M \rightarrow [M-H]^+ + RH$$

For methane, R^+ is CH_5^+ and $C_2H_5^+$, and M is a long-chain alkane. In the case of CH_5^+, the reaction proceeds to form $[M-H]^+ + CH_4 + H_2$. The spectra resulting from hydride abstraction will show an M–1 *m/z* peak resulting from the loss of H^-. This reaction is exothermic so fragmentation of the $[M-H]^+$ ion is often observed.

Often, both hydride-abstraction and proton-transfer ionization can be evident in the sample spectrum. One example is the methane CI spectrum of long-chain methyl esters, where both hydride abstraction from the hydrocarbon chain and proton transfer to the ester function occur. In the methane PCI spectrum of methyl stearate, for example, the MH^+ peak at *m/z* 299 is created by proton transfer and the $[M-1]^+$ peak at *m/z* 297 is created by hydride abstraction.

Addition

For many analytes, proton-transfer and hydride-abstraction chemical ionization reactions are not thermodynamically favorable. In these cases, reagent-gas ions are often reactive enough to combine with the analyte molecules by condensation or association (addition reactions). The resulting ions are called adduct ions. Adduct ions are observed in methane chemical ionization by the presence of $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$ ions, which result in M+29 and M+41 *m/z* mass peaks.

Addition reactions are particularly important in ammonia CI. Because the NH_3 has a high proton affinity, few organic compounds will undergo proton transfer with ammonia reagent gas. In ammonia CI, a series of ion-molecule reactions takes place, resulting in the formation of NH_4^+, $[NH_4NH_3]^+$, and $[NH_4(NH_3)_2]^+$. In particular, the ammonium ion, NH_4^+, will give rise to an intense $[M+NH_4]^+$ ion observed at M+18 *m/z*, either through condensation or association. If this resulting ion is unstable, subsequent fragmentation may be observed. The neutral loss of H_2O or NH_3, observed as a subsequent loss of 18 or 17 *m/z*, respectively, is also common.

Charge exchange

Charge-exchange ionization can be described by the reaction:

$$X^{+\bullet} + M \rightarrow M^{+\bullet} + X$$

where X^+ is the ionized reagent gas and M is the analyte of interest. Examples of reagent gases used for charge exchange ionization include the noble gases (helium, neon, argon, krypton, xenon, and radon), nitrogen, carbon dioxide, carbon monoxide, hydrogen, and other gases that do not react "chemically" with the analyte. Each of these reagent gases, once ionized, has a recombination energy expressed as:

$$X^{+\bullet} + e^- \rightarrow X$$

or simply the recombination of the ionized reagent with an electron to form a neutral species. If this energy is greater than the energy required to remove an electron from the analyte, the first reaction above is exothermic and thermodynamically allowed.

Charge-exchange chemical ionization is not widely used for general analytical applications. It can, however, be used in some cases when other chemical ionization processes are not thermodynamically favored.

Negative CI Theory

Negative chemical ionization (NCI) is performed with analyzer voltage polarities reversed to select negative ions. There are several chemical mechanisms for NCI. Not all mechanisms provide the dramatic increases in sensitivity often associated with NCI. The four most common mechanisms (reactions) are:

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

In all of the cases except the ion-molecule reactions, the reagent gas serves a function different from the function it serves in PCI. In NCI, the reagent gas is often referred to as the buffer gas. When the reagent gas is bombarded with high energy electrons from the filament, the following reaction occurs:

$$\text{Reagent gas} + e^-_{(230\ \text{eV})} \rightarrow \text{Reagent ions} + e^-_{(\text{thermal})}$$

If the reagent gas is methane (**Figure 16** on page 53), the reaction is:

$$CH_4 + e^-_{(230\ \text{eV})} \rightarrow CH_4^+ + 2e^-_{(\text{thermal})}$$

The thermal electrons have lower energy levels than the electrons from the filament. It is these thermal electrons that react with the sample molecules.

There are no negative reagent gas ions formed. This prevents the kind of background that is seen in PCI mode and is the reason for the much lower detection limits of NCI. The products of NCI can only be detected when the MS is operating in negative ion mode. This operating mode reverses the polarity of all the analyzer voltages.

Carbon dioxide is often used as a buffer gas in NCI. It has obvious cost, availability, and safety advantages over other gases.

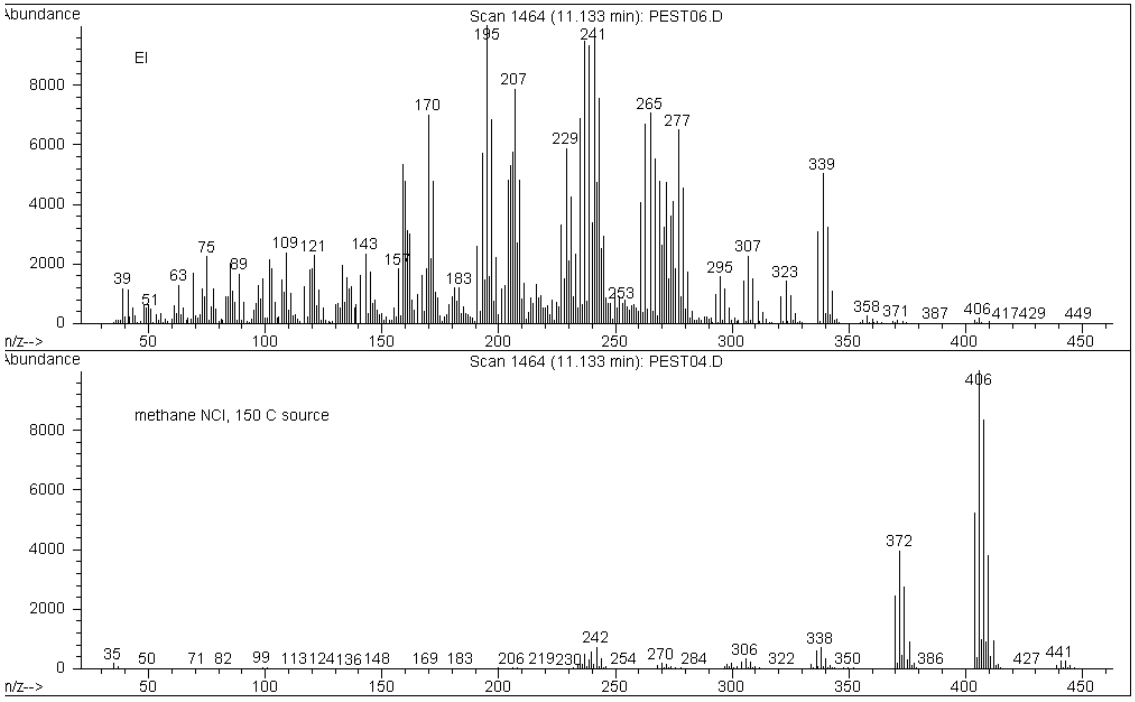

Figure 16. Endosulfan I (MW = 404): EI and methane NCI

Electron capture

Electron capture is the primary mechanism of interest in NCI. Electron capture (often referred to as high-pressure electron capture mass spectrometry or HPECMS) provides the high sensitivity for which NCI is known. For some samples under ideal conditions, electron capture can provide sensitivity as much as 10 to 1,000 times higher than positive ionization.

Note that all the reactions associated with positive CI will also occur in NCI mode, usually with contaminants. The positive ions formed do not leave the ion source because of the reversed lens voltages, and their presence can quench the electron capture reaction.

The electron capture reaction is described by:

$$MX + e^-_{(thermal)} \rightarrow MX^{-\bullet}$$

where MX is the sample molecule and the electron is a thermal (slow) electron generated by the interaction between high energy electrons and the reagent gas.

In some cases, the $MX^{-\bullet}$ radical anion is not stable. In those cases, the reverse reaction can occur:

$$MX^{-\bullet} \rightarrow MX + e^-$$

The reverse reaction is sometimes called autodetachment. This reverse reaction generally occurs very quickly. Thus, there is little time for the unstable anion to be stabilized through collisions or other reactions.

Electron capture is most favorable for molecules that have hetero-atoms. For example: nitrogen, oxygen, phosphorus, sulfur, silicon, and especially the halogens: fluorine, chlorine, bromine, and iodine.

The presence of oxygen, water, or almost any other contaminant interferes with the electron-attachment reaction. Contaminants cause the negative ion to be formed by the slower ion-molecule reaction. This generally results in less sensitivity. All potential contamination sources, especially oxygen (air) and water sources, must be minimized.

Dissociative electron capture

Dissociative electron capture is also known as dissociative resonance capture. It is a process similar to electron capture. The difference is that during the reaction, the sample molecule fragments or dissociates. The result is typically an anion and a neutral radical. Dissociative electron capture is illustrated by the reaction equation:

$$MX + e^-_{(thermal)} \rightarrow M^{\bullet} + X^-$$

This reaction does not yield the same sensitivity as electron capture, and the mass spectra generated typically have lower abundance of the molecular ion.

As with electron capture, the products of dissociative electron capture are not always stable. The reverse reaction sometimes occurs. This reverse reaction is sometimes called an associative detachment reaction. The equation for the reverse reaction is:

$$M^{\bullet} + X^{-} \rightarrow MX + e^{-}$$

Ion pair formation

Ion pair formation is superficially similar to dissociative electron capture. The ion pair formation reaction is represented by the equation:

$$MX + e^{-}_{(thermal)} \rightarrow M^{+} + X^{-} + e^{-}$$

As with dissociative electron capture, the sample molecule fragments. Unlike dissociative electron capture, however, the electron is not captured by the fragments. Instead, the sample molecule fragments in such a way that the electrons are distributed unevenly and positive and negative ions are generated.

Ion-molecule reactions

Ion-molecule reactions occur when oxygen, water, and other contaminants are present in the CI source. Ion-molecule reactions are two to four times slower than electron-attachment reactions and do not provide the high sensitivity associated with electron capture reactions. Ion-molecule reactions can be described by the general equation:

$$M + X^{-} \rightarrow MX^{-}$$

where X^{-} is most often a halogen or hydroxyl group that was created by ionization of contaminants by electrons from the filament. Ion-molecule reactions compete with electron capture reactions. The more ion-molecule reactions that occur, the fewer electron capture reactions occur.

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