HEWLETT PACKARD

HP 5973 MSD
PCI / NCI

Hardware Manual

Document History

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Warranty

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Noise Declaration

Deutsch
LpA << 70 dB am Arbeitsplatz normaler Betrieb nach EN 27779:1991

English
LpA << 70 dB operator position normal operation per ISO 7779:1988

Instrument Identification

Each HP 5973 MSD is identified by a unique 10-character serial number. This serial number is located on a label on the lower left side near the front of the instrument. On CI upgrades, a serial number is located on the flow module.

When corresponding with Hewlett-Packard about your instrument, be sure to include the model number and both full 10-character serial numbers.

Write the serial number of your HP 5973 MSD and flow module (if applicable) here for reference:

MSD serial #:

____

CI flow module serial #:

____

HP 5973 MSD version

HP 5973 MSDs are equipped with either a diffusion pump or a turbomolecular (turbo) pump. Chemical Ionization is available for the turbo MSD only. The serial number label displays a product number that tells what kind of MSD you have:

G1098A = Diffusion pump
G1099A = Turbo pump
G1999A = CI (turbo pump)

Manual Conventions

Cautions
Cautions call attention to procedures which, if not correctly performed or adhered to, could result in ***damage to the instrument***.

Warnings
Warnings call attention to procedures which, if not correctly performed or adhered to, could result in ***personal injury***.

Part Numbers
In this manual, Hewlett-Packard part numbers are generally listed in parentheses after the name of the part or in tables in the *Parts* chapter. Most Hewlett-Packard part numbers are either four-digit-by-four-digit (1234-1234) numbers or five-digit-by-five-digit (12345-12345) numbers.

A few tools and supplies listed have no part numbers and are not available from Hewlett-Packard. Most of these can be obtained from laboratory supply companies.

Safety Information

Safety Symbols (on equipment)

Refer to operating instructions

Indicates hazardous voltage

Indicates hot surface

Indicates earth (ground) terminal

Safety class
The HP 5973 Mass Selective Detector (MSD) is a Safety Class I instrument and has been designed and tested in accordance with IEC Publication 1010-1 Safety Requirements for Electrical Equipment for Measurement, Control, and Laboratory Use.

WARNING
Connecting an MSD to a power source which is not equipped with a protective earth contact creates a shock hazard for the operator and can damage the instrument. Likewise, interrupting the protective conductor inside or outside the MSD or disconnecting the protective earth terminal creates a shock hazard for the operator and can damage the instrument.

WARNING
Make sure that only fuses with the required current rating and of the specified type are used for replacement. The use of incorrect or makeshift fuses or the short-circuiting of fuse holders creates a shock hazard for the operator and can damage the instrument.

WARNING
Any adjustment, maintenance or repair of the opened instrument while it is connected to a power source should be avoided if possible and, if required, should be carried out only by trained persons who are aware of the hazards involved.

Safety Information continued on the inside of the back cover.

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General Information

General information

This manual contains information pertaining to the operation, and maintenance of the HP 5973 CI MSD. It is intended to be used in addition to the HP 5973 MSD Hardware Manual. The CI hardware consists of a chemical ionization source, GC/MSD interface, a reagent gas mass flow controller, and associated electronics. Setup and tuning macros are included with the data system software. CI Autotune uses perfluoro-5,8-dimethyl-3,6,9-trioxidodecane (PFDTD) as a calibrant and methane as the reagent gas.

Chapter 1 provides a list of the CI performance specifications and a list of reagent gases.

Chapter 2 presents some basics of the theory of chemical ionization and the advantages it offers.

Chapter 3 describes the CI hardware components and their functions.

Chapter 4 provides instructions for using CI.

Chapter 5 discusses problems most likely to be encountered and their probable causes.

Chapter 6 discusses routine maintenance procedures.

Chapter 7 provides information about parts that are available for maintenance of the CI hardware.

Specifications

This section lists the principal performance specifications for the HP G1999A (HP 5973 MSD with *factory-installed* CI.) These specifications are subject to change without notice. These specifications do not apply to CI upgrades; see the upgrade installation documents.

Sensitivity, Scan

Positive CI: 75:1 RMS for 1 µl of 100 pg/µl Benzophenone (*m/z* = 183.1)
Negative CI: 500:1 RMS for 1 µl of 1 pg/µl Octafluoronapthalene (*m/z* = 272.0)

Sensitivity, SIM

Positive CI: 10:1 RMS for 1 µl of 100 fg/µl Benzophenone (*m/z* = 183.1)
Negative CI: 10:1 RMS for 1 µl of 1 fg/µl Octafluoronapthalene (*m/z* = 272.0)

NOTE Installation does not include demonstration of SIM sensitivity.

Reagent gases and regulators

The following reagent gases and hardware may be required for operation of CI with the HP 5973 MSD (depending on your choice of reagent). Use the highest purity gases available. Do not use gases of less than the listed purity. The hardware items listed below are available from Matheson and Swagelok. They are representative of products that are appropriate for the purpose.

A gas purifier (G1999-80410) is needed for use with methane and isobutane; it cannot be used with ammonia. A separate purifier is necessary for each gas supply.

Methane (required)

Lecture bottle (0.06 m^3, 56 liters), UHP 99.97%
Regulator 3320
Stand, model J05
Swagelok female connector, SS-200-7-2

Isobutane (optional)

Lecture bottle (0.17 kg), instrument, 99.5% purity
Regulator 3321 or 3320
Stand, model J05
Swagelok female connector, SS-200-7-2

Ammonia (optional)

Lecture bottle (0.17 kg), anhydrous, 99.99% purity
Regulator 3332
Stand, model J05
Swagelok female connector, SS-200-7-4

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Hardware Reference

Description

The chemical ionization (CI) hardware allows the HP 5973 MSD to operate in the positive and negative CI modes (PCI and NCI) and produce high-quality, classical CI spectra, which include molecular adduct ions. A variety of reagent gases (including methane, isobutane, and ammonia) can be used.

The HP 5973 CI system adds to the HP 5973 MSD:

- CI ion source
- Redesigned EI/CI GC/MSD interface
- Interface tip seal
- Reagent gas flow control module
- Bipolar HED power supply
- Updated GC/MSD ChemStation software

A triode high vacuum gauge controller (HP 59864B) is ***not*** included, but is ***required*** for operation in CI mode.

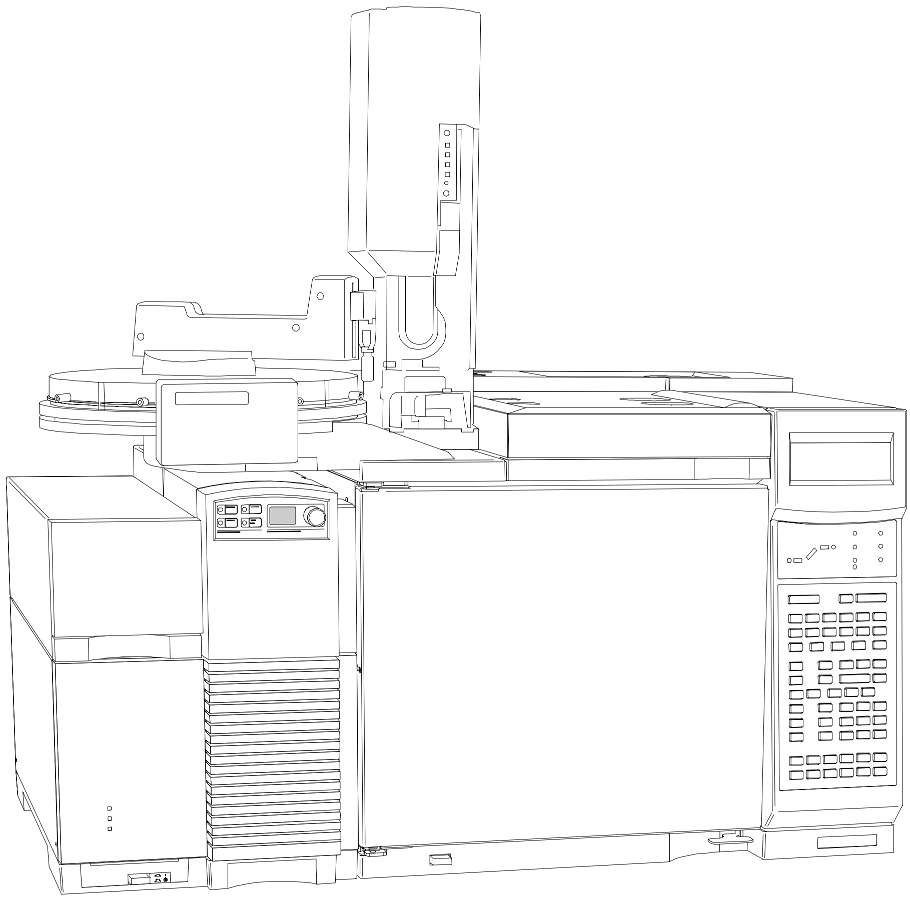
To achieve the relatively high source pressure required for CI while still maintaining high vacuum in the quadrupole and detector, the MSD CI system has been carefully optimized. Special seals along the flow path of the reagent gas and very small openings in the source ensure that all the source gases stay in the source long enough for the appropriate chemical reactions to occur.

The CI interface has special plumbing for reagent gas. The interface can be used for both EI and CI operation. A spring-loaded insulating seal fits onto the tip of the interface to seal the opening to the ion source; this seal ***must*** be removed before installing the EI source.

Switching back and forth between CI and EI takes less than an hour, although a 1– to 2–hour wait is ***required*** in order to purge the reagent gas lines and bake out water and other contaminants.

The CI source, CI interface, and reagent gas control module are described in more detail in the remainder of this chapter.

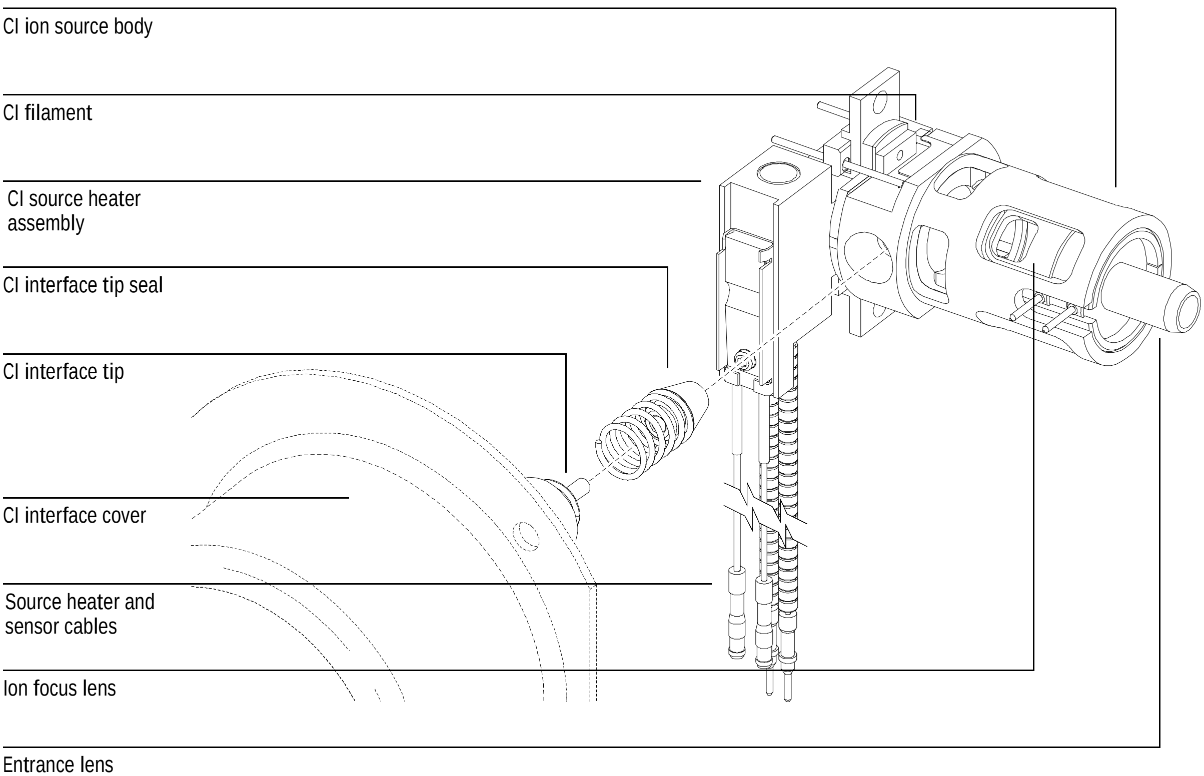
To help assure quality of reagent gas entering the system, a methane/isobutane gas purifier is provided, and is required. It removes oxygen, water, hydrocarbons, and sulfur compounds.

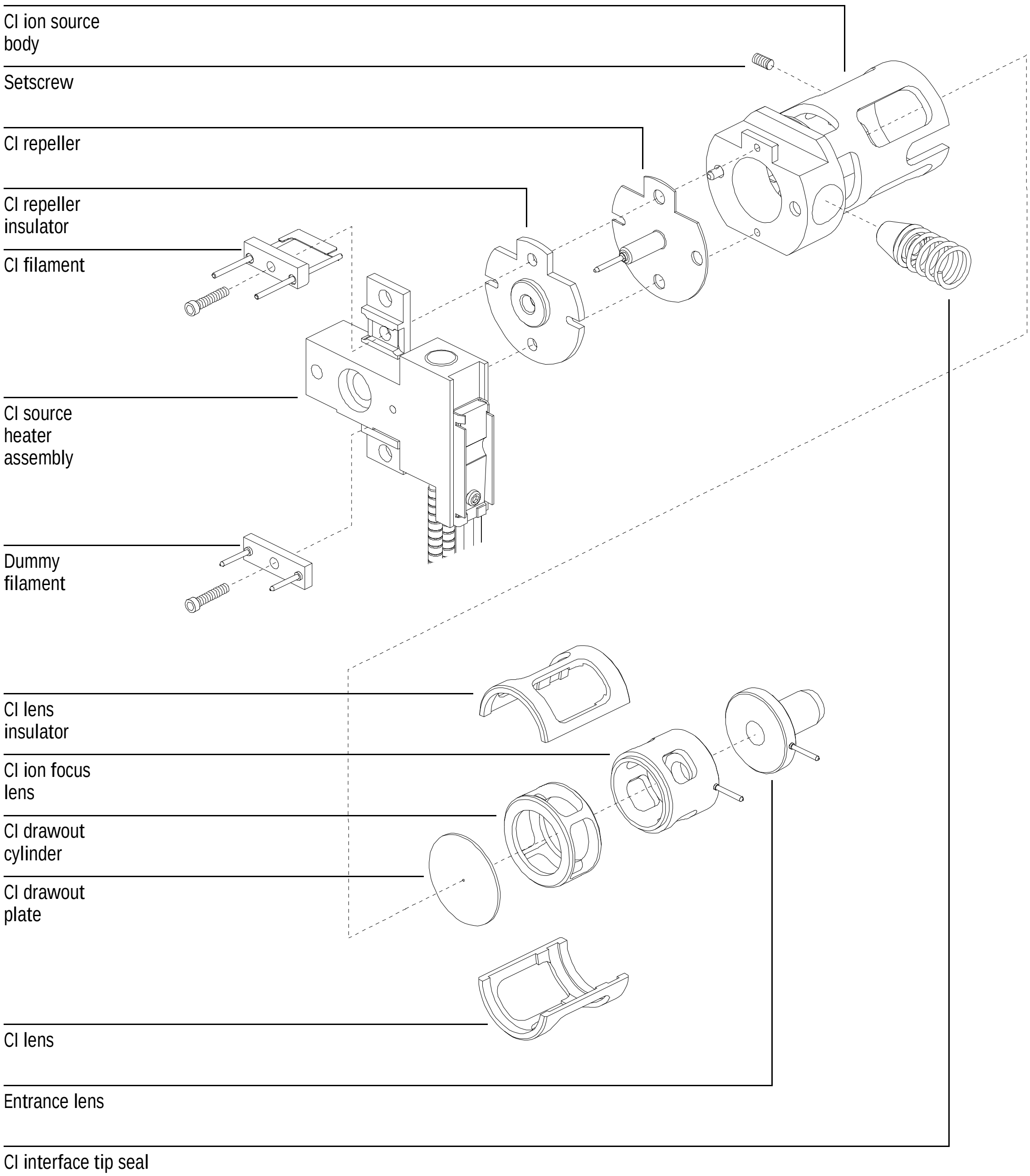


CI ion source

The CI ion source is similar to the EI source, but only has one part in common with the EI source — the entrance lens. The single CI filament has a straight wire and a reflector. There is a “dummy” filament to provide connections for the other wires.

The holes in the ion 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 ion source. Large slots in the drawout cylinder and ion-source body provide enhanced pumpout for the ion source optics.



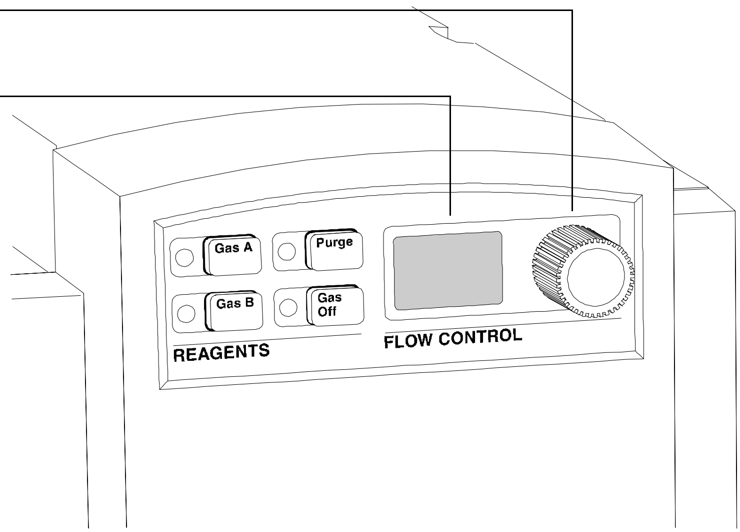

CI ion source body
Setscrew
CI repeller
CI repeller insulator
CI filament
CI source heater assembly
Dummy filament
CI lens insulator
CI ion focus lens
CI drawout cylinder
CI drawout plate
CI lens
Entrance lens
CI interface tip seal

Reagent gas flow control module

The CI reagent gas flow control module regulates the flow of reagent gas into the EI/CI GC/MSD interface. The flow control module consists of a mass flow controller (MFC), gas select valves, CI calibration valve, isolation valve, control panel, control and display electronics, and plumbing. The back panel provides Swagelok inlet fittings for methane and one other reagent gas. The other fittings in the flow module are VCR fittings; VCR fittings have a disposable gasket that must be replaced every time the seal is opened. Operation of the flow module is through the control panel on the front. **Gas A** must be plumbed with Methane. **Gas B** can be plumbed with any other reagent gas.
Operation of the flow module is through the control panel on the front.

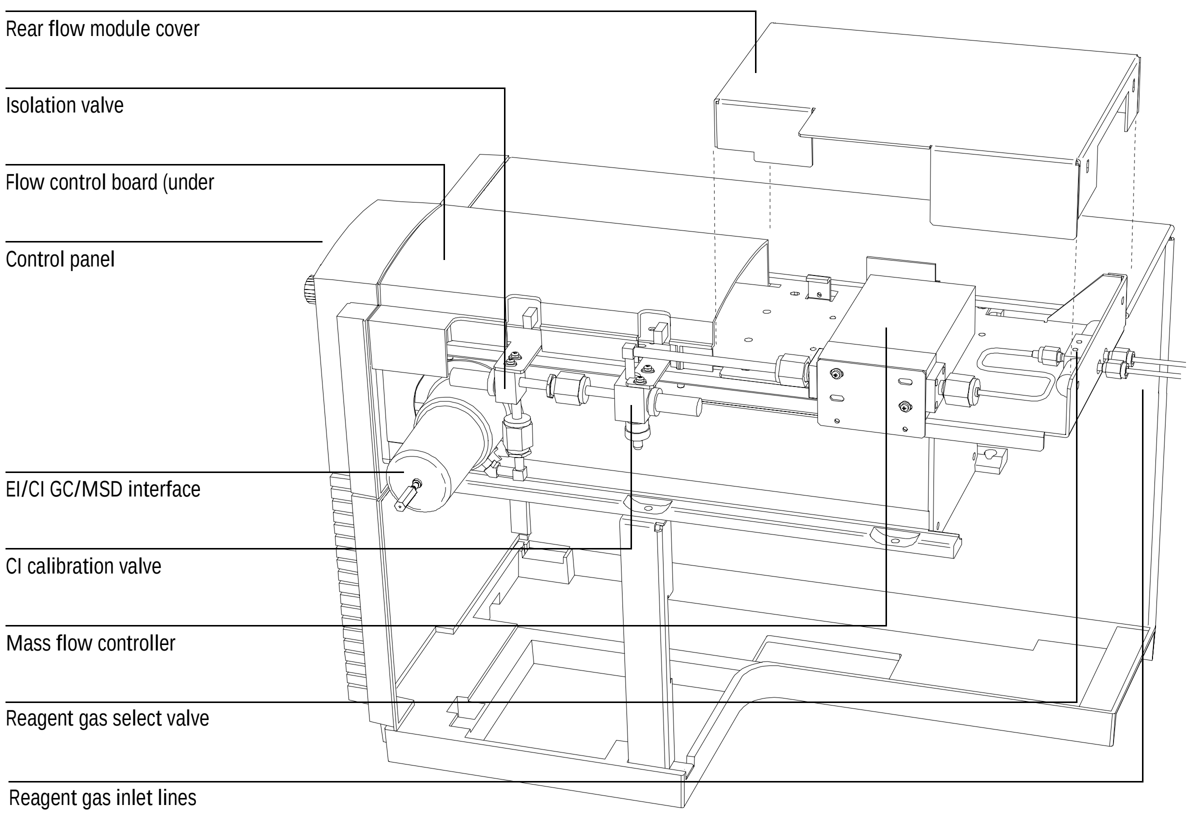
Flow control knob

Flow control display



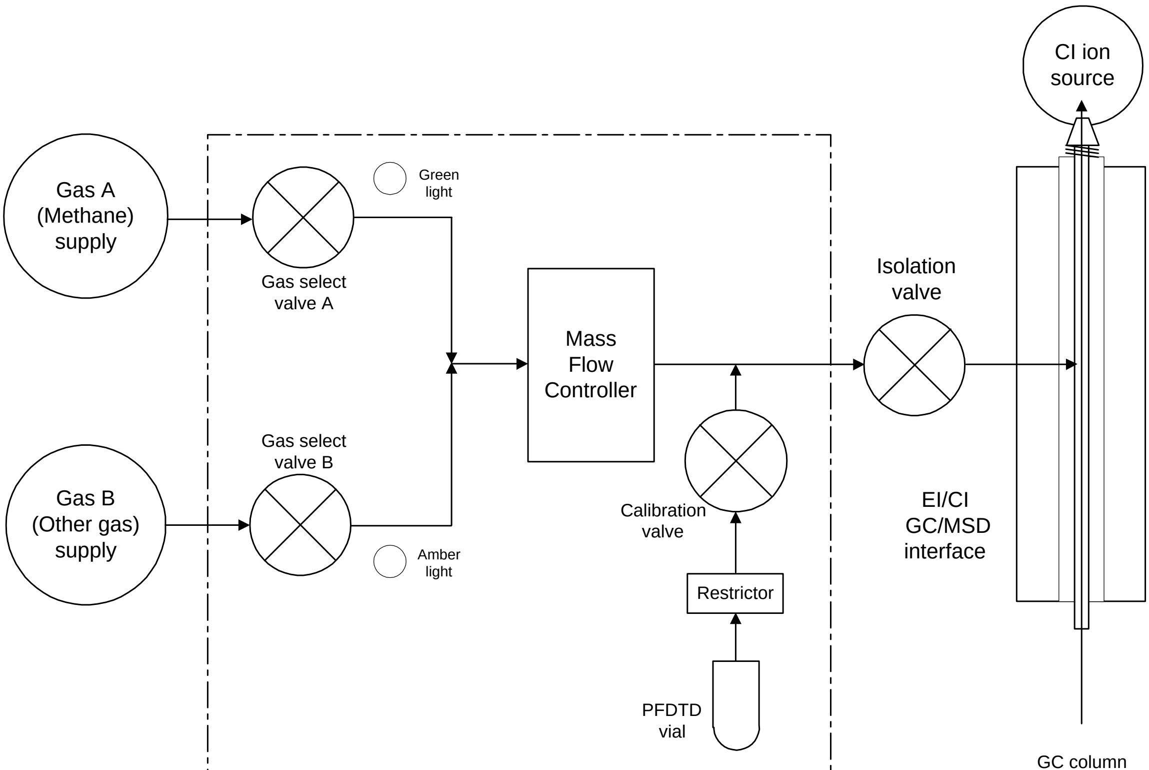
- Each button on the control pane has an LED (light) next to it. When that button is active, the light is on.
- **Gas A** or **Gas B** opens the chosen gas select valve. Only one can be open at a time.
- **Gas Off** closes the gas select and isolation valves. **Gas Off** also sets the MFC to 0% flow, unless **Purge** is on. The **Gas Off** LED must be off to turn on **Gas A** or **Gas B**
- The flow control knob is used to adjust the flow. When no gases are turned on the Flow Control display will show dashes: ––.
- **Purge** sets the MFC to 100% of total flow (fully open), regardless of the position of the flow control knob or the state of the select valves.

- The flow control display shows the gas flow as a percentage of the total possible flow (5 ml/min for ***methane***).
- The flow control knob adjusts the gas flow. If the selected flow rate can not be achieved or maintained, the numbers in the flow control display will flash.
- The CI calibration valve is controlled by the ChemStation software, and opens automatically during CI autotune or manual tuning, allowing PFDTD to diffuse into the ion source.
- The isolation valve prevents contamination of the flow control module by atmosphere while the MSD is vented or by PFTBA during EI operation.



CAUTION

Try to avoid tuning any more often than absolutely necessary to minimize PFDTD background and ion source contamination.



Reagent gas flow control module schematic

When you turn off one gas and turn on the other, the system sets a 6-minute delay with **Gas Off** and **Purge** both on to pump out the flow control module. The light for the selected reagent gas will flash, indicating the delay timer is active. Once the delay is finished, the **Purge** and **Gas Off** lights will turn off, and the light for the selected gas will stop flashing and stay on.

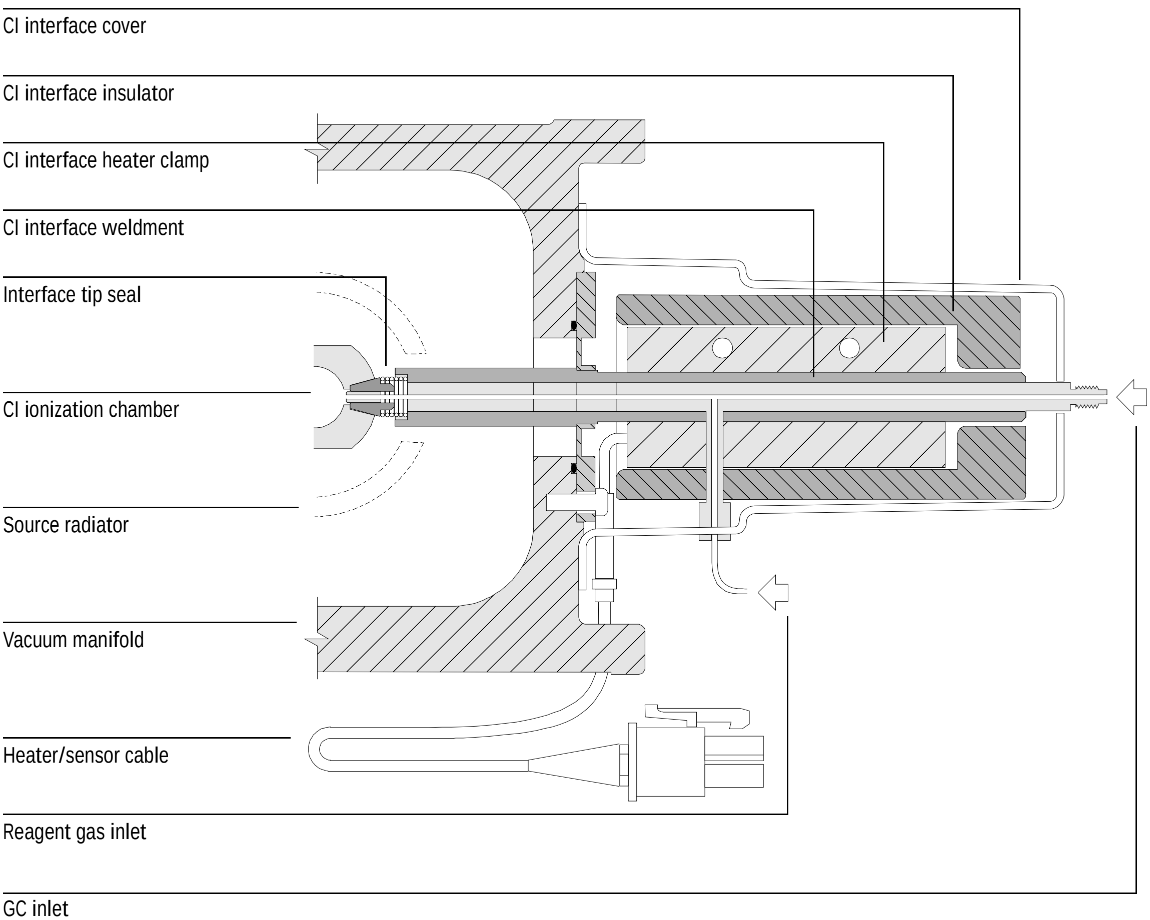
When the MSD is turned off, all valves are closed, and all lights are off. At startup, all valves are closed and all lights are off, except **Gas Off**.

The flow control board remembers the flow setting for each gas. When either gas is selected, the control board automatically sets the same flow that was used for that gas last time.

Flow control module state diagram:						
Result	Gas A flows	Gas B flows	Purge with Gas A	Purge with Gas B	Pump out flow module	Standby, vented, or EI mode
Control panel lights (LEDs)						
Gas A (green)	On	Off	On	Off	Off	Off
Gas B (amber)	Off	On	Off	On	Off	Off
Purge (red)	Off	Off	On	On	On	Off
Gas Off (red)	Off	Off	Off	Off	On	On
Valve state						
Valve A	Open	Closed	Open	Closed	Closed	Closed
Valve B	Closed	Open	Closed	Open	Closed	Closed
MFC	On → setpoint	On → setpoint	On → 100%	On → 100%	On → 100%	Off (→0%)
Isolation valve	Open	Open	Open	Open	Open	Closed

EI/CI GC/MSD interface (CI interface)

The CI interface mounts onto the side of the vacuum manifold, with one end in the GC oven and the other in the MSD. Reagent gas is plumbed into the interface. The tip of the interface assembly extends into the ionization chamber. A spring-loaded seal keeps reagent gases from leaking out around the tip. The reagent gas is plumbed into the interface body, and mixes with carrier gas and sample in the ion source. This interface is also used for EI operation in CI MSDs.



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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 that is 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 collisionally 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 ion 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 may decrease 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 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 positive chemical ionization at ion source pressures in the 0.8 – 2.0 Torr range. These are:

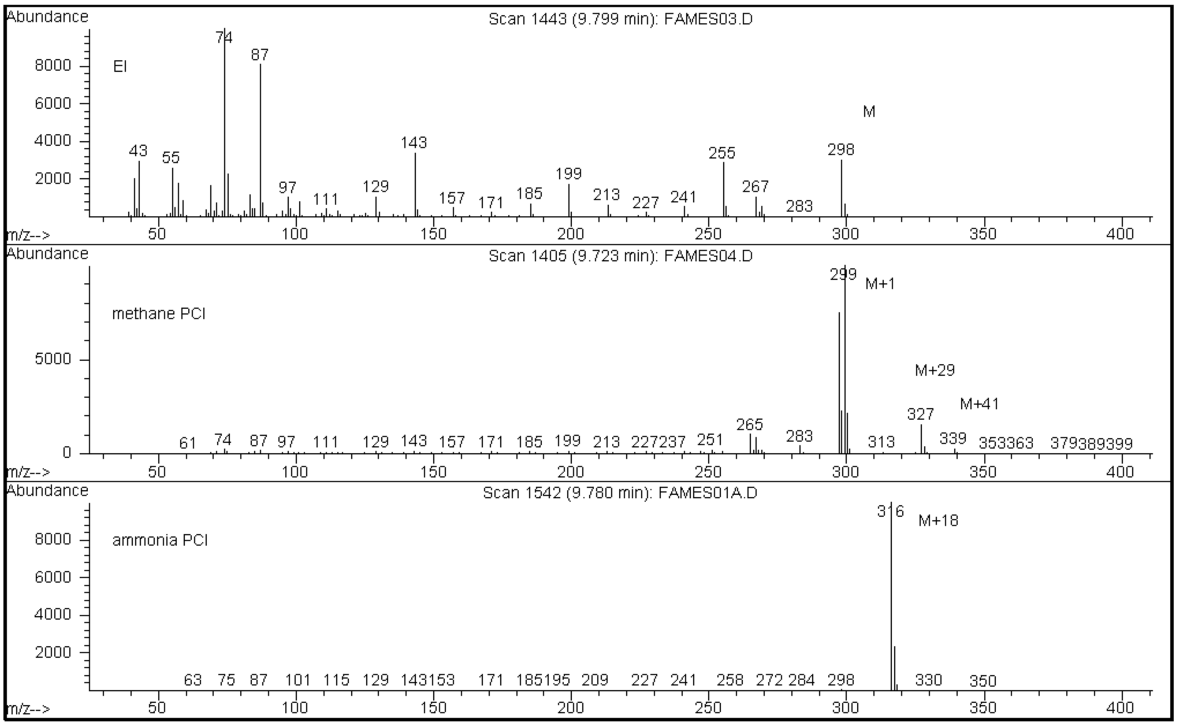
- Proton transfer
- Hydride abstraction
- Addition
- Charge exchange

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 opposite. 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.

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, then the protonated reagent gas will transfer its proton to the analyte, forming a positively 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. The following tables 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 extent of the softness is dependent on the proton affinities of both the analyte and the reagent gas, as well as on other factors, including ion source temperature.

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)
i-C_4H_{10}	195	t-$C_4H_9^+$ (*m/z* 57)
NH_3	207	NH_4^+ (*m/z* 18)

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	l80
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^-, then 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

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

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 $[M\text{-}H]^+ + CH_4 + H_2$. The spectra resulting from hydride abstraction will show an M-1 amu peak resulting from the loss of H . This reaction is exothermic so fragmentation of the $[M\text{-}H]^+$ 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 $[M\text{-}1]^+$ 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 amu 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 amu, 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 amu, 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, then 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 negative chemical ionization. Not all mechanisms provide the dramatic increases in sensitivity often associated with negative chemical ionization. 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 positive chemical ionization. In negative CI, 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:

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

If the reagent gas is methane, the reaction is:

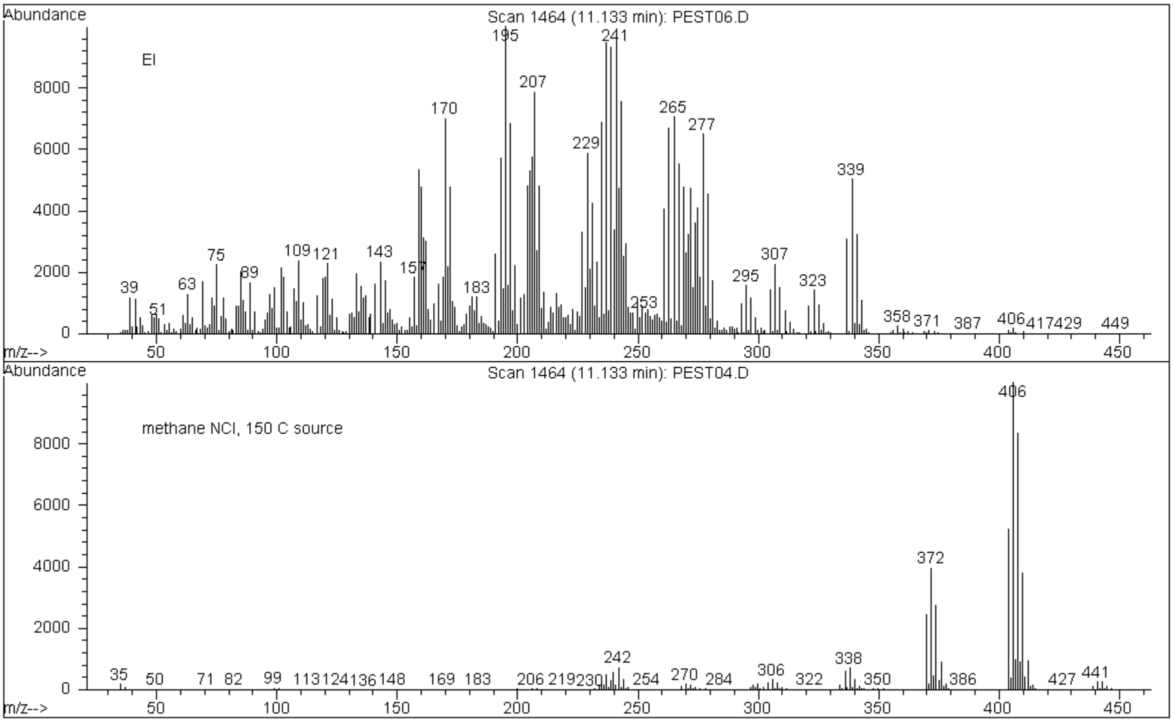
$$CH_4 + e^-_{(230eV)} \rightarrow CH_4^+ + 2e^-_{(thermal)}$$

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 negative chemical ionization can only be detected when the MSD 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 negative CI. It has obvious cost, availability, and safety advantages over other gases.

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



Electron capture

Electron capture, is the primary mechanism of interest in negative CI. 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, and under ideal conditions, electron capture can provide sensitivity as much as 10 to 1000 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 ion source. Ion-molecule reactions are 2 – 4 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 has been 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.

4

CI setup

CI hardware setup

This chapter provides information and instructions about setting up the HP 5973 CI MSD hardware for operation in CI mode. The following topics are covered in this chapter

- Venting and pumping down the CI MSD
- Installing the GC column in the CI interface
- Installing the CI ion source
- Installing the CI interface tip seal
- Switching between operating modes

The following chapter provides information on setting up the software and operating the CI MSD in CI mode.

CI setup

In setting up your CI MD for operation in CI mode requires special care to avoid contamination and air leaks.

General guidelines

- Before venting in EI mode, verify that the GC/MSD system is performing correctly.
- Make sure the carrier gas plumbing and GC have no air leaks. (EI mode.)
- Make sure the MSD vacuum system has no air leaks.
- Make sure the reagent gas inlet line(s) are equipped with gas purifiers (not applicable for ammonia.)
- Use extra-high purity reagent gases; 99.97% or better for methane and as pure as is available for other reagent gases.

To vent the CI MSD

Software changes

This procedure is the same as in the HP 5973 MSD Hardware Manual except for the following details. See the MSD reference Collection CD-ROM for a video of this procedure.

1 **Switch off the HP 59864B triode gauge controller.**

2 **In Diagnostics/Vacuum Control view, select Vent from the Vacuum menu. Follow the instructions presented.**

The software will instruct you to press the Gas Off button to turn off the reagent gas flow and close the isolation valve. The software will prompt you when it is safe to switch off the power.

WARNING **If you are using hydrogen as a carrier gas, the carrier gas flow must be off before turning off foreline pump, to prevent hydrogen from accumulating in the MSD. Read the *Hydrogen Carrier Gas Safety Guide* (5955-5398) before operating the MSD with hydrogen carrier gas.**

CAUTION Be sure the GC oven and the MSD are cool before turning off carrier gas flow.

WARNING **When the MSD is vented, do not put the ChemStation into Top view -- this will turn on the interface heater.**

CAUTION The **Gas Off** light must be on when the MSD is venting or pumping down, and during EI operation.

WARNING **Allow the analyzer to cool to near room temperature before touching it.**

To remove the CI MSD covers

Materials needed: Screwdriver, Torx T-15 (8710-1622)
Screwdriver, Torx T-10 (8710-1623)

The analyzer cover is removed for venting and for many maintenance procedures. The side cover is removed to access the electronics module. See the MSD reference Collection CD-ROM for a video of this procedure.

CI analyzer cover

1 **Grasp the front of the analyzer cover and lift up enough to disengage the front latch.**

2 **Reach back and grasp the back edge of the analyzer cover.**

3 **Pull forward to disengage the spring latch.**

It may take a firm pull to disengage the latch.
To replace the cover, reverse the above steps.

Side cover

4 **Remove the analyzer cover.**

5 **Remove the 3 Torx T-15 screws that hold the MSD side cover in place.**

6 **Move the cover left slightly to disengage it and then pull it straight forward.**

To replace the cover, reverse the above steps.

To pump down the MSD

Software changes

The software is revised periodically. If the steps in this procedure do not match your MSD ChemStation software, refer to the manuals and online help supplied with the software for more information.

WARNING

Make sure your MSD meets *all* the conditions listed in the introduction to the Operation chapter of the HP 5973 MSD Hardware Manual (page 32) before starting up and pumping down the MSD. Failure to do so can result in personal injury.

WARNING

If you are using hydrogen as a carrier gas, do not start carrier gas flow until the MSD has been pumped down. If the vacuum pumps are off, hydrogen will accumulate in the MSD and an explosion may occur. Read the *Hydrogen Carrier Gas Safety Guide* (5955-5398) before operating the MSD with hydrogen carrier gas.

1 **Select Diagnostics/Vacuum Control from the View menu.**

2 **Select Pump Down from the Vacuum menu.**

3 **When prompted, switch on the MSD and click OK.**

4 **Press lightly on the side plate to ensure a correct seal.**

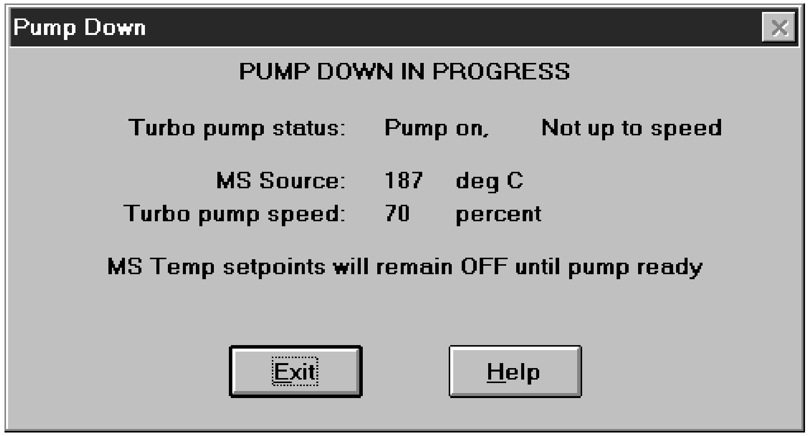
The rough pump will make a gurgling noise. This noise should stop within a minute. If the noise continues, there is a ***large*** air leak in your system, probably at the interface column nut, the vent valve, or the side plate seal.

Within 10 to 15 minutes the diffusion pump should be hot, or the turbo pump speed up to 80%. The turbo pump speed should eventually reach 95%. If the MSD does not pump down correctly, see the manual or online help for information on troubleshooting air leaks and other vacuum problems.

5 **The software will prompt you to turn on the GC/MSD interface heater and GC oven. Click OK when you have done so.**

6 **Load the tune file PCICH4.U, if you are running in CI mode, or ATUNE.U if you are running in EI mode.**

7 **Accept the temperature setpoints.**



CAUTION

Do not turn on any heated zones until carrier gas flow is on. Heating a column with no carrier gas flow will damage the column.

8 **Reinstall the MSD analyzer cover.**

The analyzer cover was removed during the vent procedure.

9 **Verify that GC carrier gas flow is on.**

10 **Check vacuum gauge controller to verify that the pressure is decreasing.**

11 **Press Gas A and Purge, and verify that the Gas A and Purge lights are on.**

12 **Verify that PCICH4.U is loaded, and accept the temperature setpoints.**

13 **Set the GC/MSD interface to 320°C.**

14 **Purge for at least one hour.**

15 **Press the Purge button to turn off Purge.**

16 **Set Gas A to 20%.**

17 **Let system bake out for at least 2 hours. For best NCI sensitivity, bake out overnight.**

To install the GC column in the EI/CI GC/MSD interface

Materials needed:

Adjustment tool (G1099-20030)
Ferrules
- 0.27-mm id, for 0.10-mm id columns (5062-3518)
- 0.37-mm id, for 0.20-mm id columns (5062-3516)
- 0.40-mm id, for 0.25-mm id columns (5181-3323)
- 0.47-mm id, for 0.32-mm id columns (5062-3514)
- 0.74-mm id, for 0.53-mm id columns (5062-3512)

Interface column nut (05988-20066)
Wrench, 1/4-inch open-end (8710-0510)

See the MSD reference Collection CD-ROM for a video of this procedure.

1 **Put an interface nut and a conditioned ferrule on the column and push the column into the adjustment tool.**

2 **Trim about 1 cm from the end of the column.**

3 **Pull the column back until the tip of the column is even with the end of the tool, or extends less than one mm past the end.**

The column should not extend more than 1 mm past the tip of the adjustment tool.

4 **Using two 1/4-inch wrenches, tighten the nut.**

Tighten only enough so that the column does not slip in the ferrule if tugged gently.

5 **Loosen the nut and remove the column from the tool.**

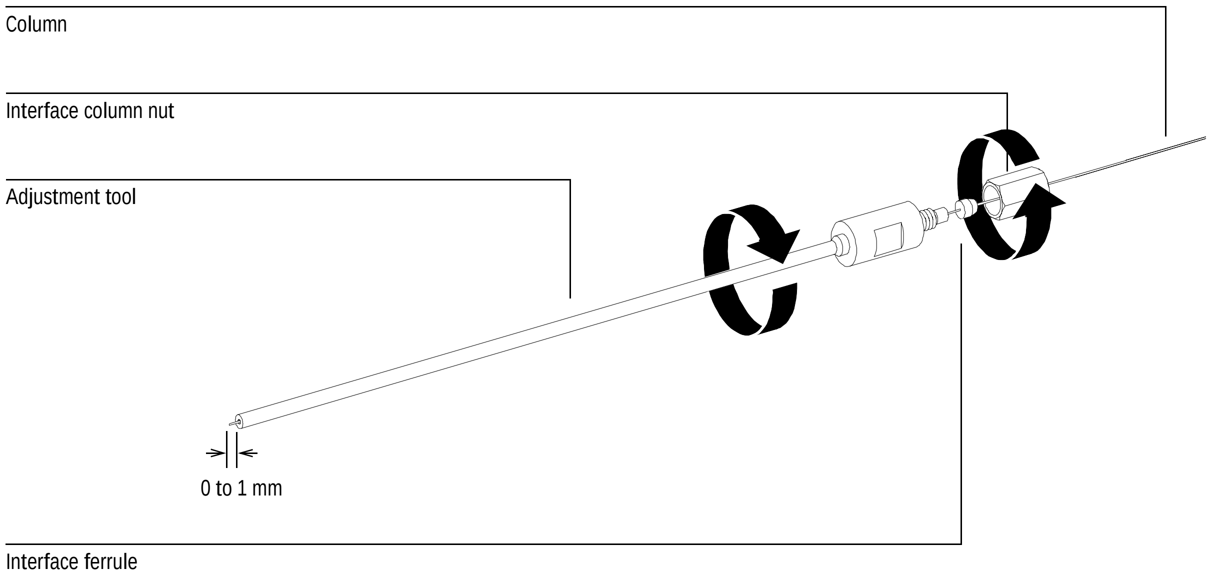
6 **install the column in the GC/MSD interface.**

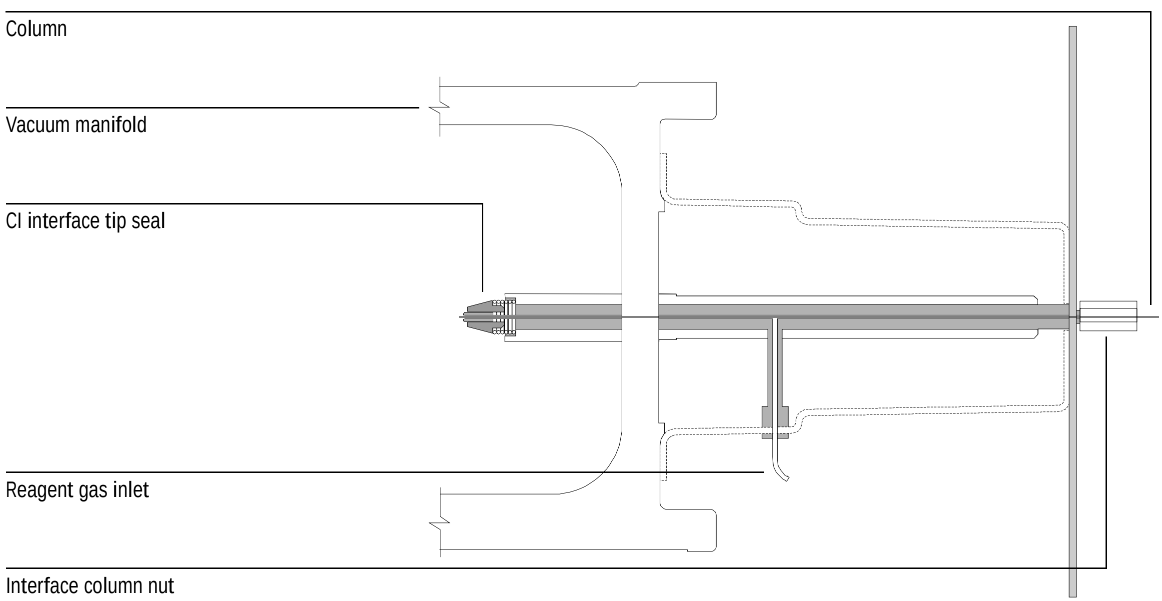
Note that the EI/CI interface doesn't extend quite as far into the GC oven as the EI interface does.

NOTE The EI/CI interface doesn't extend quite as far into the GC oven as the EI interface did.

7 **Using two 1/4-inch wrenches, tighten the nut.**

Do not overtighten. Tighten only until the ferrule squeaks.


Column
Interface column nut
Adjustment tool
0 to 1 mm
Interface ferrule


Column
Vacuum manifold
CI interface tip seal
Reagent gas inlet
Interface column nut

To switch from CI to EI operating mode

1 **Press the Gas Off button to close the isolation valve.**

2 **Vent the MSD. See page See page 38.**

The software will prompt you for the appropriate actions.

3 **Open the analyzer**

4 **Remove the CI interface tip seal. See page 48.**

5 **Remove the CI ion source. See page 46.**

6 **Install the EI ion source**

7 **Place the CI ion source and interface tip seal in the in the ion source storage box**

8 **Pump down the MSD. See page 40.**

CAUTION

Always wear clean gloves while touching the analyzer or any other parts that go inside the vacuum manifold.

CAUTION

Electrostatic discharges to analyzer components are conducted to the side board where they can damage sensitive components. Wear a grounded anti-static wrist strap (see page 98 of the HP 5973 MSD Hardware Manual) and take other anti-static precautions ***before*** you open the vacuum manifold.

To switch from EI to CI operating mode

Always set up the CI MSD in PCI first, even if you are going to run NCI.

1 **Vent the MSD. See page 38.**

2 **Open the analyzer.**

3 **Remove the EI ion source.**

CAUTION

Electrostatic discharges to analyzer components are conducted to the side board where they can damage sensitive components. Wear a grounded anti-static wrist strap (see page 98 of the HP 5973 MSD Hardware Manual) and take other anti-static precautions ***before*** you open the vacuum manifold.

4 **Install the CI ion source. See page 46.**

5 **Install the interface tip seal. See page 48.**

6 **Close the analyzer.**

7 **Pump down the MSD. See page 40.**

To install the CI ion source

CAUTION

Electrostatic discharges to analyzer components are conducted to the side board where they can damage sensitive components. Wear a grounded anti-static wrist strap and take other anti-static precautions ***before*** you open the vacuum manifold.

1 **Remove the EI ion source.**

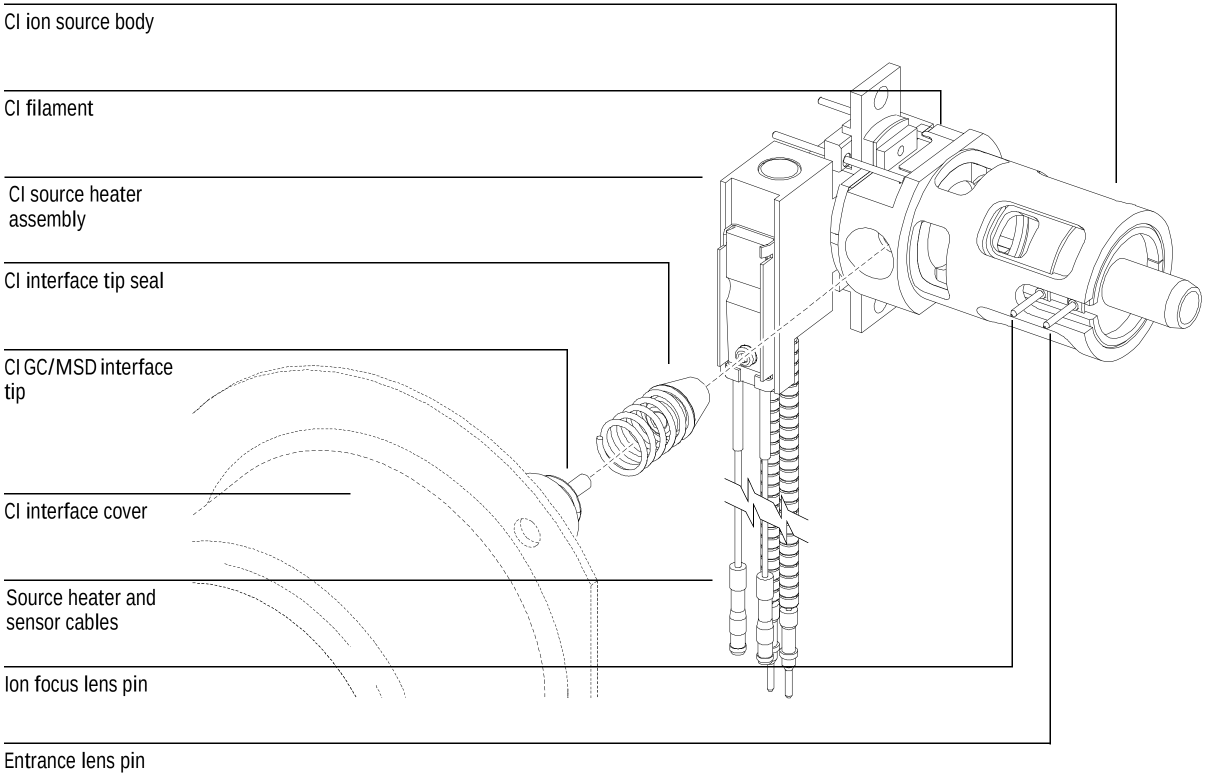
2 **Remove the CI ion source from its storage box and insert the ion source into the radiator.**

3 **Reinstall the thumbscrews.**

4 **Connect the dummy filament, repeller, and CI filament wires.**

5 **Connect the blue wire to the entrance lens pin and the orange wire to the ion focus lens pin.**

6 **Connect the heater and sensor cables.**


CI ion source body
CI filament
CI source heater assembly
CI interface tip seal
CI GC/MSD interface tip
CI interface cover
Source heater and sensor cables
Ion focus lens pin
Entrance lens pin

To install the CI interface tip seal

Materials needed: Interface tip seal (G1099-60412)

The interface tip seal must be in place for CI operation. It is necessary to achieve adequate ion source pressure for CI.

CAUTION Electrostatic discharges to analyzer components are conducted to the side board where they can damage sensitive components. Wear a grounded anti-static wrist strap and take other anti-static precautions ***before*** you open the vacuum manifold.

1 **Vent the MSD and open the analyzer. See page 38.**

2 **Remove the seal from the ion source storage box.**

3 **Place the seal over the end of the interface. See the illustration on page 49.**

To remove the seal, reverse the above steps.

4 **Verify that the CI ion source is installed.**

5 ***Gently* check the alignment of the analyzer and the interface.**

When the analyzer is aligned correctly, the analyzer can be closed all the way with no resistance except the spring tension from the interface tip seal.

CAUTION Forcing the analyzer closed if these parts are misaligned will damage the seal or the interface or the ion source, or will keep the sideplate from sealing.

6 **You can align the analyzer and interface by wiggling the sideplate on its hinge.**

If the analyzer still won’t close, contact your Hewlett-Packard service representative.

The figure opposite shows the alignment of the interface, tip seal, and CI ion source.

5

CI operation

CI Operation

This chapter provides information and instructions about operating an HP 5973 CI MSD in CI mode. Most of the material is related to methane chemical ionization but one section discusses the use of other reagent gases. The following topics are covered in this chapter

- Setting the reagent gas flow to optimize the pressure in the CI source
- Checking for air leaks
- PCI and NCI autotunes
- Verify sensitivity performance

NOTE Sequencing is not appropriate for automating methods that use different reagent gases or gas flows, as these parameters must be set ***manually***.

Tuning macros, beginning tune files, and menus for CI operation are included with the updated ChemStation software. The software provides instructions for setting the reagent gas flow and for performing CI autotunes.

Autotunes are provided for PCI with methane reagent gas and for NCI with any reagent gas.

CI operation

Operating your MSD in the CI mode is slightly more complicated than operating in the EI mode. After tuning, gas flow, source temperature, and electron energy may need to be optimized for your specific analyte.

General guidelines

- Make sure the CI ion source and GC/MSD interface tip seal are installed.
- Make sure the reagent gas plumbing has no air leaks. This is determined in PCI mode, checking for *m/z* 32 after the methane pre-tune.
- Set ion source temperature to 150°C for negative CI, and 250°C for PCI. Set quadrupole temperature to 106°C for both modes.
- Set the GC/MSD interface temperature to 320°C for PCI, and 280°C for NCI.

Start the system in PCI mode first.

By bringing the system up in PCI mode first, you will be able to do the following:

- Check the interface tip seal by looking at the *m/z* 28 to 27 ratio (in the methane flow adjust panel.).
- Tell if a gross air leak is present by monitoring the ions at *m/z*19(water), 32.
- Confirm if the MS is generating “real” ions and not just background noise.

It is nearly impossible to perform any diagnostics on the system in NCI. In NCI, there are no reagent gas ions to monitor for any gas. It is difficult to diagnose an air leak and difficult to tell whether a good seal is being created between the interface and the ion volume.

To set up the software for CI operation

1 **Switch to the Manual Tune view.**

2 **Select Load Tune Values from the File menu**

3 **Select the tune file PCICH4.U.**

4 **If CI autotune has never been run for this tune file, the software will prompt you through a series of dialog boxes. *Accept the default values unless you have a very good reason for changing anything.***

The tune values have a dramatic effect on MSD performance. Always start with the default values when first setting up for CI, and then make adjustments for your specific application. See the table below for default values for the Tune Control Limits box.

.

Default Tune Control Limits (used by CI autotune only. These limits should *not* be confused with the parameters set in Edit MS Parameters, or with those appearing on the tune report.)

Reagent gas	**Methane**		**Isobutane**[a]		**Ammonia**[a]	
Ion polarity	Positive	Negative[a]	Positive[a]	Negative[a]	Positive[a]	Negative[a]
Abundance target[b],	$1x10^6$	$1x10^6$	N/A[c]	$1x10^6$	N/A[c]	$1x10^6$
Peakwidth target[d]	0.6	0.6	N/A[c]	0.6	N/A[c]	0.6
Maximum repeller	4	4	N/A[c]	4	N/A[c]	4
Maximum emission current[e]	240	50	N/A[c]	50	N/A[c]	50
Max electron energy, eV	240	240	N/A[c]	240	N/A[c]	240

a. Always set up in PCI with methane first, then switch to your desired ion polarity and gas.

b. Adjust higher or lower to get desired signal abundance. Higher signal abundance also gives higher noise abundance. This is adjusted for data acquisition by setting the EMV in the method.

c. There are no PFDTD ions formed in PCI with any reagent gas but methane, hence, CI autotune is not available with these configurations.

d. Higher peakwidth values give better sensitivity, lower values give better resolution.

e. Optimum emission current maximum for NCI is very compound-specific, and must be selected empirically. Optimum emission current for pesticides, for example, may be about 200µA.

To set up methane reagent gas flow

The reagent gas flow must be adjusted for maximum stability before tuning the CI system. Do the ***initial*** setup with methane in positive ion mode (PCI). No flow adjustment procedure is available for NCI, as no negative reagent ions are formed.

Adjusting the methane reagent gas flow is a three-step process: setting the flow control to 20%, pre-tuning on the reagent gas ions, and adjusting the flow for stable reagent ion ratios, for methane, *m/z* 28/27.

Your data system will prompt you through the flow adjustment procedure.

CAUTION After the system has been switched from EI to CI mode, or vented for any other reason, the MSD must be baked out for at least 2 hours before tuning.

1 **Press the Gas A button. Verify that only the Gas A light is on.**

2 **Adjust the flow to 20%**

3 **Check the vacuum gauge controller to verify correct pressure. See page 62.**

4 **Select Methane Pretune from the Setup menu.**

The methane pretune tunes the instrument for optimum monitoring of the methane reagent ion *m/z* 28/27 ratio.

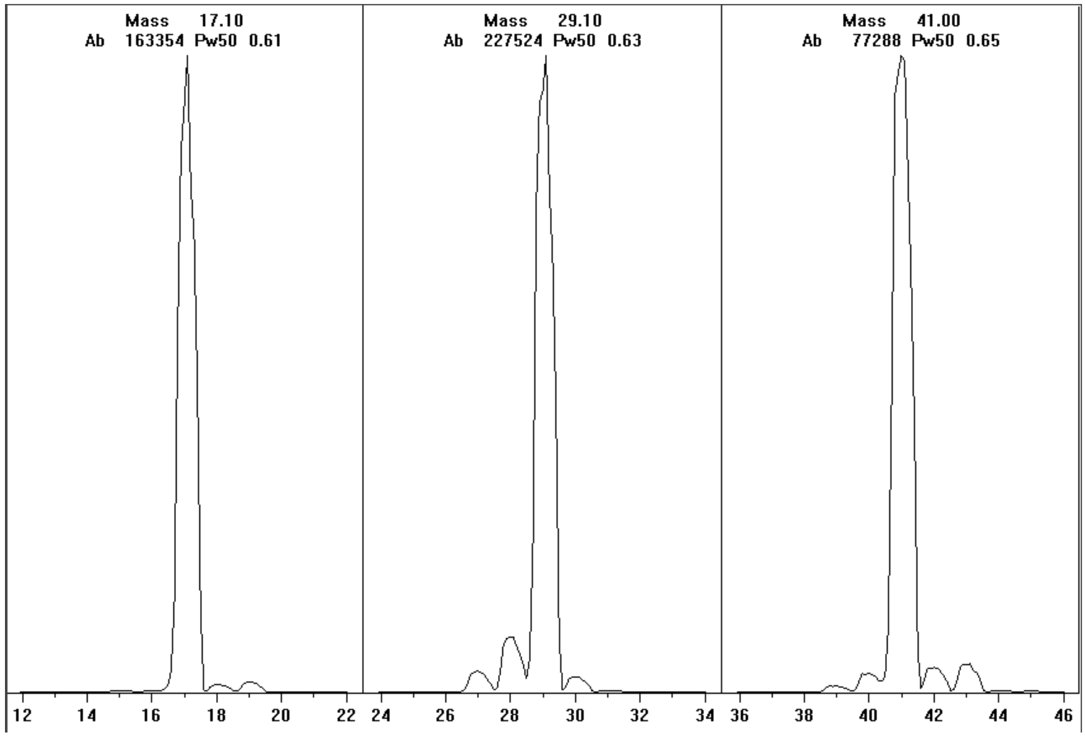
5 **Examine the displayed profile scan of the reagent ions.**

- Make sure there is no visible peak at *m/z* 32. A peak there indicates an air leak. If such a peak is present, find and repair the leak before proceeding. Operating in the CI mode with an air leak will rapidly contaminate the ion source.
- Make sure that the peak at *m/z* 19 (protonated water) is not larger than the peak at *m/z* 17.

6 **Perform the Methane Flow Adjust.**

Adjust the methane flow to get the ratio of m/z 28:27 between 1.5 and 5.0.

CAUTION Continuing with CI autotune if the MSD has an air leak or large amounts of water will result in ***severe*** ion source contamination. If this happens, you will need to ***vent the MSD*** and ***clean the ion source***.



Methane pre-tune after more than a day of baking out. Note the low abundance of *m/z* 19 and absence of any visible peak at *m/z* 32. Your MSD will probably show more water, but the abundance of *m/z* 19 should still be less than that of *m/z* 17.

To perform CI autotune

After the reagent gas flow is adjusted, the lenses and electronics of the MSD should be tuned. Perfluoro-5,8-dimethyl-3,6,9-trioxidodecane (PFDTD) is used as the calibrant. Instead of flooding the entire vacuum chamber, the PFDTD is introduced directly into the ionization chamber through the GC/MSD interface by means of the gas flow control module.

CAUTION

After the system has been switched from EI to CI mode, or vented for any other reason, the MSD must be baked out for at least 2 hours before tuning. Longer bakeout is recommended before running samples for optimal sensitivity.

There is a PCI autotune for methane only, as there are no PFDTD ions produced by other gases in positive mode. PFDTD ions are visible in NCI for any reagent gas. Always tune for methane PCI first regardless of which mode or reagent gas you wish to use for your analysis.

Default (starting) CI tune parameters)

Reagent gas	**Methane**		**Isobutane**		**Ammonia**		**EI**
Ion polarity	Positive	Negative	Positive	Negative	Positive	Negative	N/A
Emission	150 µA	50 µA	150 µA	50 µA	150 µA	50 µA	35 µA
Electron energy	150 eV	150eV	150eV	150eV	150eV	150eV	70
Filament	1	1	1	1	1	1	1 or 2
Repeller	3 V	3 V	3 V	3 V	3 V	3 V	30 V
Ion focus	130 V	130 V	130 V	130 V	130 V	130 V	90 V
Entrance lens (gain)	0 mV/amu	0 mV/amu	0 mV/amu	0 mV/amu	0mV/amu	0 mV/amu	0 mV/amu
Entrance lens offset	20V	20	20V	20	20V	20	25
EMVolts	1200	1200	1200	1200	1200	1200	1200
Gas Off	Off	Off	Off	Off	Off	Off	On
Gas select valve	A	A	B	B	B	B	N/A
Suggested flow	20%	40%	20	40	20	40	N/A
Source temp	250°C	150°C	250°C	150°C	250°C	150°C	230°C
Quad temp	106°C	106°C	106°C	106°C	106°C	106°C	150°C
Interface temp	320°C	280°C	320°C	280°C	320°C	280°C	280°C
Autotune	Yes	Yes	No	Yes	No	Yes	Yes

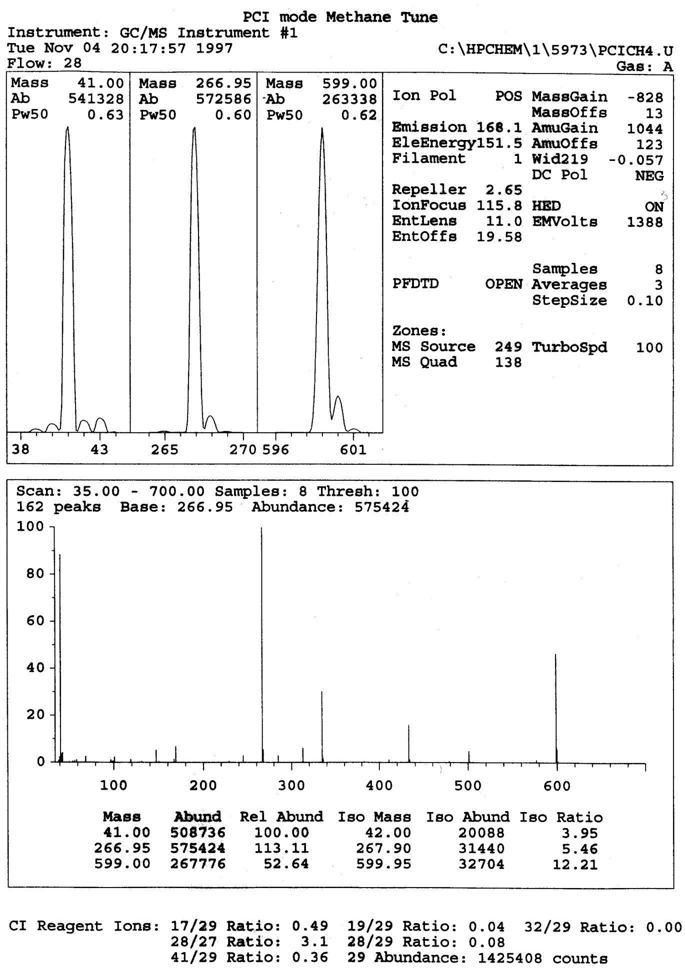
To perform a positive CI autotune (methane only)

1 Load the PCICH4.U tune file. Accept the default settings.

2 Perform methane setup. See page 54.

3 Under the Tune menu, click CI Autotune.

There are no tune performance criteria. If autotune completes, it passes.



To perform a negative CI autotune (any reagent gas)

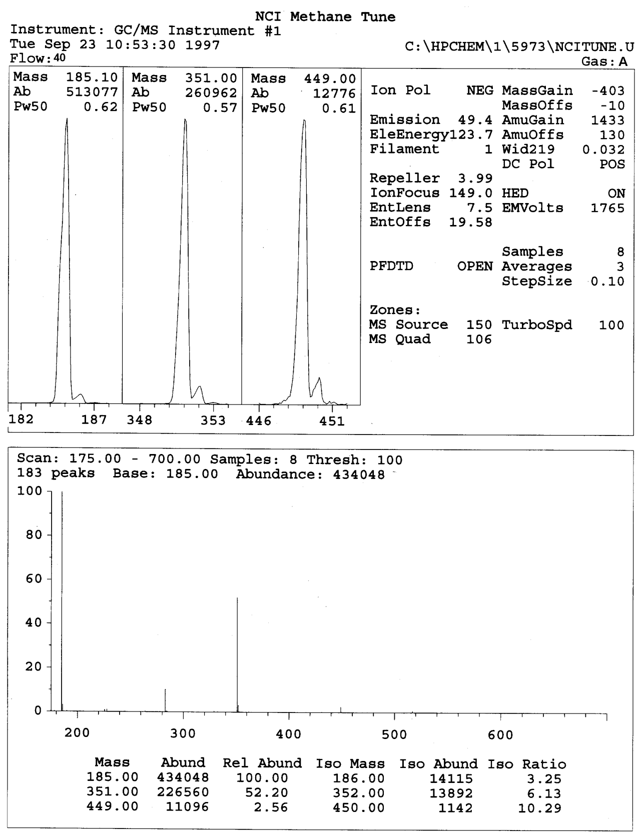
1 Load NCICH4.U (or an existing tune file for the reagent gas you are using).

Accept the default temperature and other settings.

2 If you don't already have an NCI tune file for your reagent gas, click Select Reagent Gas under the Setup menu, and click on the gas you are using.

3 Under the Tune menu, click CI Autotune.

There are no tune performance criteria. If autotune completes, it passes.



To verify positive CI performance

Materials needed: Benzophenone, 100 pg/µl (8500-5440)

1 **Verify that the PCICH4.U tune file is loaded.**

2 **On the flow control panel, turn Purge off, and set Gas A to 20% flow.**

3 **In Manual Tune view, perform CI setup. See page 54.**

4 **Run CI Autotune. See page 56.**

5 **Run the PCI sensitivity method: BENZ_PCI.M, using 1 µl of 100pg/µl Benzophenone.**

6 **Verify that S:N > 75:1 RMS**

To verify negative CI performance

Materials needed: OFN, 1 pg/µl (8500-5441)

1 **Verify that the MSD performs correctly in EI mode.**

2 **Load the NCICH4.U tune file, and accept the temperature setpoints.**

3 **Turn Purge and Gas A on and let the system stabilize for 90 minutes.**

4 **Turn Purge off, and set Gas A to 40% flow.**

5 **In Manual Tune view, run CI Autotune.** **See page 60.**

Note that there are no criteria for a "passing" Autotune in CI. If the Autotune completes, it passes.

6 **Run the NCI sensitivity method: OFN_NCI.M using 1 µl of 1 pg/ml OFN.**

7 **Verify that S/N > 500:1 RMS.**

To operate the reagent gas flow control module

For a video demonstration of the gas flow control module, see the HP 5973 MSD Reference Collection CD-ROM.

Flow control module state diagram:

Result	Gas A flows	Gas B flows	Purge with Gas A	Purge with Gas B	Pump out flow module	Standby, vented, or EI mode
Control panel lights (LEDs)						
Gas A (green)	On	Off	On	Off	Off	Off
Gas B (amber)	Off	On	Off	On	Off	Off
Purge (red)	Off	Off	On	On	On	Off
Gas Off (red)	Off	Off	Off	Off	On	On
Valve state						
Valve A	Open	Closed	Open	Closed	Closed	Closed
Valve B	Closed	Open	Closed	Open	Closed	Closed
MFC	On → setpoint	On → setpoint	On → 100%	On → 100%	On → 100%	Off (→0%)
Isolation valve	Open	Open	Open	Open	Open	Closed

To monitor high vacuum pressure

Materials needed: Gauge controller (HP 59864B)
Triode gauge cable (8120-6573)

WARNING **Never connect or disconnect the cable from the triode gauge tube while the MSD is under vacuum. Risk of implosion and injury due to broken glass exists.**

WARNING **If you are using hydrogen as a carrier gas, do not turn on the triode gauge tube if there is any possibility that hydrogen has accumulated in the manifold. The triode gauge filament can ignite hydrogen. Read the *Hydrogen Carrier Gas Safety Guide* (5955-5398) before operating the MSD with hydrogen carrier gas**

1 **Connect the gauge controller to the triode gauge tube. See page 100.**

2 **Start up and pump down the MSD. See page 40.**

3 **Switch on the power switch on the back of the gauge controller.**

4 **Press and release the GAUGE button.**

After a few seconds, the pressure should be displayed.

Pressure is displayed in the format **X.X – X** where **– X** is the base 10 exponent. Units are Torr.

The gauge controller will not turn on if the pressure in the MSD is above approximately 8×10^{-3} Torr. The gauge controller will display all 9s and then go blank. The triode gauge tube can measure pressures between approximately 8×10^{-3} and 3×10^{-6} Torr. The gauge controller is calibrated for nitrogen, but all pressures listed in this manual are for helium.

The largest influence on operating pressure is the carrier gas (column) flow. The following table lists typical pressures for various helium carrier gas flows. These pressures are approximate and will vary from instrument to instrument.

Typical pressure readings

Use the HP 59823B high-vacuum gauge controller. Note that the mass flow controller is calibrated for methane, and the high vacuum gauge controller is calibrated for helium, so these measurements are not accurate, but are intended as a guide to typical observed readings. They were taken with the following set of conditions. Note that these are typical PCI temperatures:

Source temperature	250°C
Quad temperature	106°C
Interface temperature	320°C
Helium carrier gas flow	1ml/min

MFC (%)	Pressure (Torr)		
	Methane	Isobutane	Ammonia
10	5.6×10^{-5}	6.5×10^{-5}	4.7×10^{-5}
15	7.7×10^{-5}	9.2×10^{-5}	6.7×10^{-5}
20	9.8×10^{-5}	1.2×10^{-4}	8.5×10^{-5}
25	1.2×10^{-4}	1.4×10^{-4}	1.0×10^{-4}
30	1.4×10^{-4}	1.8×10^{-4}	1.2×10^{-4}
35	1.6×10^{-4}	2.0×10^{-4}	1.4×10^{-4}
40	1.8×10^{-4}	2.3×10^{-4}	1.6×10^{-4}
45	2.0×10^{-4}	2.6×10^{-4}	1.9×10^{-4}
50	2.2×10^{-4}	3.0×10^{-4}	2.1×10^{-4}
60	2.7×10^{-4}	3.5×10^{-4}	2.5×10^{-4}

Familiarize yourself with the measurements on ***your*** system under operating conditions, and watch for ***changes*** that may indicate a vacuum or gas flow problem.

To use other reagent gases

This section describes the use of isobutane or ammonia as the reagent gas. You should be familiar with operating the CI-equipped HP 5973 MSD with methane reagent gas before attempting to use other reagent gases.

CAUTION

Do not use nitrous oxide as a reagent gas. It radically shortens the life span of the filament.

Changing the reagent gas from methane to either isobutane or ammonia changes the chemistry of the ionization process and yields different ions. The principal chemical ionization reactions encountered were described in general in the *Theory of operation* section in Chapter 2. If you are not experienced with chemical ionization, we suggest reviewing that material before you proceed.

NOTE

Not all setup operations can be performed in all modes with all reagent gases. See the following table for details.

Reagent gas/ mode	Reagent ion masses	Flow adj ions: Ratio	PFDTD Calibrant ions
Methane/ PCI	17, 29, 41[a]	28/27: 1.5 – 5.0	41, 267, 599
Methane/ NCI	17, 35, 235[b]	N/A	185, 351, 449
Isobutane/ PCI	39, 43, 57	57/43: 5.0 – 30.0	N/A
Isobutane/ NCI	17, 35, 235	N/A	185, 351, 449
Ammonia/ PCI	18, 35, 52	35/18: 0.1 – 1.0	N/A
Ammonia/ NCI	17, 35, 235	N/A	185, 351, 517

a. There are no PFDTD ions formed with any reagent gas but methane. Tune with methane and use the same parameters for the other gas.

b. There are no negative reagent gas ions formed. To pretune in negative mode, use background ions: 17 (OH^-), 35 (Cl^-), and 235 (ReO_3^-). These ions can not be used for reagent gas flow adjustment. Set flow to 40% for NCI and adjust as necessary to get acceptable results for your application.

Isobutane CI

Isobutane (C_4H_{10}) is commonly used for chemical ionization when less fragmentation is desired in the chemical ionization spectrum. This is because the proton affinity of isobutane is higher than that of methane; hence, less energy is transferred in the ionization reaction. Addition and proton transfer are the ionization mechanisms most often associated with isobutane. The sample itself influences which mechanism dominates.

Ammonia CI

Ammonia (NH_3) is commonly used for chemical ionization when less fragmentation is desired in the chemical ionization spectrum. This is because the proton affinity of ammonia is higher than that of methane; hence, less energy is transferred in the ionization reaction. Because many compounds of interest have insufficient proton affinities, ammonia chemical-ionization spectra often result from the addition of NH_4^+ and then, in some cases, from the subsequent loss of water. Ammonia reagent ion spectra have principal ions at *m/z* 18, 35, and 52, corresponding to NH_4^+, $NH_4(NH_3)^+$, and $NH_4(NH_3)_2^+$.

To adjust your MSD for isobutane or ammonia chemical ionization, use the following procedure:

1 **Perform a standard Positive CI autotune with methane and PFDTD.**

2 **Under the Setup menu, click Select Reagent Gas and select Isobutane or Ammonia.**

This will change the menus to use the selected gas, and select appropriate default tune parameters.

3 **Select an new tune file name, or load an existing PCI tune file for the specific gas.**

4 **Turn Gas B on.**

After the amber light stops flashing and the Purge light goes off, set the gas flow to 20%.

5 **Click Isobutane (or Ammonia) Flow Adjust on the Setup menu.**

There is no CI autotune for isobutane or ammonia in PCI.

6 **If you wish to run NCI with isobutane or ammonia, load NCICH4.U, or load an existing NCI tune file for the specific gas.**

CAUTION

Use of ammonia affects the maintenance requirements of the MSD. See the maintenance chapter for more information.

CAUTION

The pressure of the ammonia supply must be less than 5 psig. Higher pressures can result in ammonia condensing from a gas to a liquid.

Always keep the ammonia tank in an upright position. Coil the ammonia supply tubing into several vertical loops by wrapping the tubing around a can or bottle. This will help keep any liquid ammonia out of the flow module.

Ammonia tends to break down vacuum pump fluids and seals. Ammonia CI makes more frequent vacuum system maintenance necessary.

CAUTION

When running ammonia for five or more hours a day, the foreline pump must be ballasted for at least one hour a day to minimize damage to pump seals. See page 96. Always purge the MSD with methane after flowing ammonia.

Frequently, a mixture of 5% ammonia and 95% helium or 5% ammonia and 95% methane is used as a CI reagent gas. This is enough ammonia to achieve good chemical ionization while minimizing its negative effects.

Carbon dioxide NCI

Carbon dioxide is often used as a buffer gas for negative CI. It has obvious advantages of availability and safety.

6

Troubleshooting

Troubleshooting

This chapter outlines the troubleshooting of HP 5973 MSDs equipped with PCI/NCI. Most of the troubleshooting information in the *HP 5973 MSD Hardware Manual (G1099-90001)* also applies to MSDs equipped with the CI accessory.

Common CI-specific problems

Because of the added complexity of the parts required for CI, there are many potential problems added. By far the greatest number and most serious problems with CI are associated with leaks or contamination in the reagent gas introduction system. NCI is especially sensitive to the presence of air, and air leaks that cause no problems in PCI can destroy NCI sensitivity.

As with EI, if the MSD tunes well, and no air leak is present, sample sensitivity problems should be addressed by GC injection port maintenance first.

- Wrong reagent gas
- Reagent gas not hooked up or hooked up to wrong reagent gas inlet port
- Wrong ions entered in tune file
- Wrong tune file selected
- Not enough bake-out time has elapsed since vent (background is too high)
- Wrong column positioning (extending > 1mm past tip of interface.)
- Interface tip seal not installed
- EI source installed in CI mode
- EI filament or other EI source parts in CI ion source
- Air leaks in reagent gas flow path
- CI filament has stretched and sagged:
  High EMV
  Linear (no inflection point) electron energy (EleEnergy) ramp.

Troubleshooting tips and tricks

The following are general rules for troubleshooting, with specific CI examples.

Rule 1: "Look for what has been changed."

Many problems are introduced accidentally by human actions. Every time any system is disturbed, there is a chance of introducing a new problem.

- If the MSD was just pumped down, suspect air leaks or incorrect assembly.
- If the reagent gas bottle or gas purifier were just changed, suspect leaks or contaminated or incorrect gas.
- If the GC column was just replaced, suspect air leaks or contaminated or bleeding column.
- If you have just switched ion polarity or reagent gas, suspect the tune file you have loaded in memory -- is it the appropriate file for your mode of operation?

***Rule 2: "If* complex *isn't working, go back to* simple."**

A complex task is not only more difficult to perform, but also more difficult to troubleshoot as well. For example, CI requires more parts to work correctly than EI does, and all those additional parts

- If you're having trouble with NCI, verify that PCI still works.
- If you're having trouble with other reagent gases, verify that methane still works.
- If you're having trouble with CI, verify that EI still works.

Rule 3: "Divide and conquer."

This technique is known as "half-split" troubleshooting. If you can isolate the problem to only part of the system, it is much easier to locate.

- To isolate an air leak, start by shutting the gas select valve while leaving the isolation valve and MFC open (turn on **Purge** and **Gas Off**.) If abundance of *m/z* 32 decreases, the problem is "upstream" of the flow module.

Air leaks

How do I know if I have an air leak?

Large air leaks can be detected by vacuum symptoms: loud gurgling noise from the foreline pump, inability of the turbo pump to reach 95% speed, or, in the case of smaller leaks, high pressure readings on the high vacuum gauge controller.

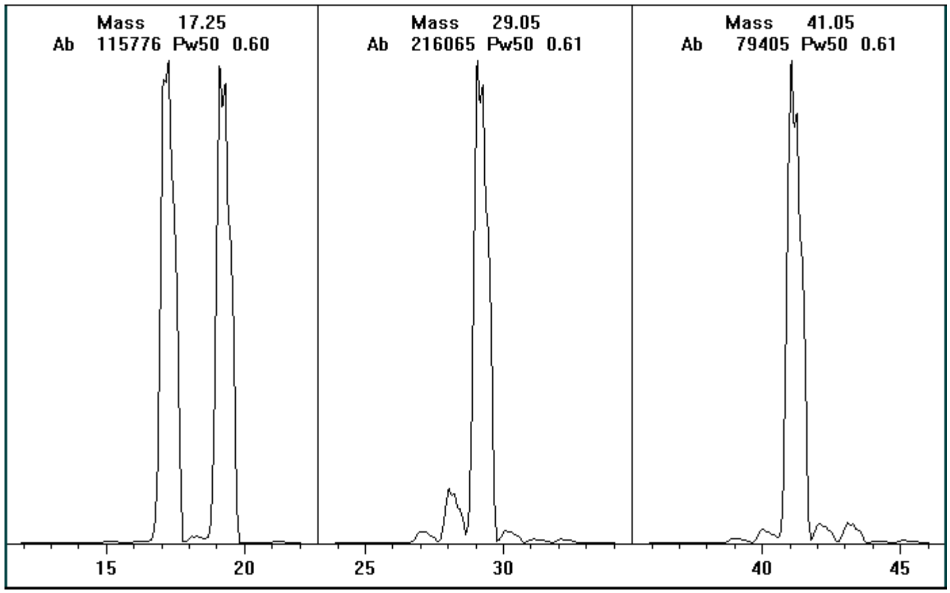
Note that the mass flow controller is calibrated for methane, and the high vacuum gauge controller is calibrated for helium, so these measurements are not accurate in absolute terms, but are intended as a guide to typical observed readings. They were taken with the following set of conditions:

Source temperature	250°C
Quad temperature	106°C
Interface temperature	320°C
Helium carrier gas flow	1ml/min

MFC (%)	**Pressure (Torr)**		
	Methane	**Isobutane**	**Ammonia**
10	5.6×10^{-5}	6.5×10^{-5}	4.7×10^{-5}
15	7.7×10^{-5}	9.2×10^{-5}	6.7×10^{-5}
20	9.8×10^{-5}	1.2×10^{-4}	8.5×10^{-5}
25	1.2×10^{-4}	1.4×10^{-4}	1.0×10^{-4}
30	1.4×10^{-4}	1.8×10^{-4}	1.2×10^{-4}
35	1.6×10^{-4}	2.0×10^{-4}	1.4×10^{-4}
40	1.8×10^{-4}	2.3×10^{-4}	1.6×10^{-4}
45	2.0×10^{-4}	2.6×10^{-4}	1.9×10^{-4}
50	2.2×10^{-4}	3.0×10^{-4}	2.1×10^{-4}
60	2.7×10^{-4}	3.5×10^{-4}	2.5×10^{-4}

Always look for small air leaks when setting up methane flow. Run the ***methane*** pre-tune. The abundance of *m/z* 19 (protonated water) should be less than that of *m/z* 17. If the MSD was just pumped down, look for the abundance of *m/z* 19 to be decreasing.

There should not be any peak visible at *m/z* 32 (O_2). This almost always indicates an air leak.



Special negative CI notes

Since NCI is so extremely sensitive, air leaks that are not detectable in EI or PCI can cause sensitivity problems in NCI. To check for this kind of air leak in NCI, inject OFN. The base peak should be at m/z 272. If the abundance of m/z 238 is much greater than that of m/z 272, you have an air leak.

How do I find the air leak?

1 Look for the last seal that was disturbed.

- If you just pumped down the MSD, press on the sideplate to check for proper seal. Poor alignment between the analyzer and the GC/MSD interface seal can prevent the sideplate from sealing.
- If you just replaced the reagent gas bottle or gas purifier, check the fittings you just opened and refastened.

2 Check for tightness of seals at injection port and interface column nuts.

Ferrules for capillary columns often loosen after several heat cycles. Do not overtighten the interface nut.

3 If any of the VCR fittings in the flow module have been loosened and then retightened, the gasket must be replaced. These gaskets are good for one use only.

CAUTION Do not loosen the nuts on any VCR fittings unless you intend to replace the gaskets. Otherwise, you *will* create an air leak.

4 Remember that most small air leaks visible in CI mode are located in either the carrier gas or reagent gas flow paths.

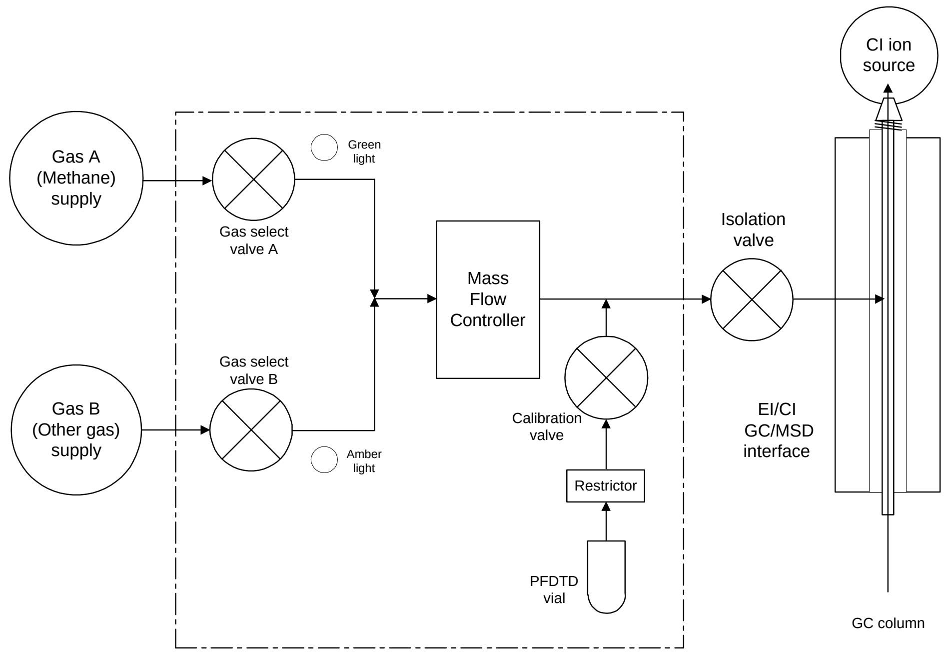
Leaks into the vacuum manifold are not likely to be seen in CI because of the higher pressure inside the ionization chamber.

5 Half-split the system.

- By closing valves starting at the gas select valves (**Gas Off** and **Purge** turned on), then moving farther “downstream” to the isolation valve (**Gas Off** turned on and **Purge** turned off.)
- You can cool and vent the MSD, remove the GC column, and cap off the interface.

If you are used to using argon or other introduced gas to find air leaks, note that this does not work well for the reagent gas flow system — it takes as long as 15 minutes for the peak to reach the ion source if the leak is at the inlet to the flow module.

Schematic of CI flow control module



Flow module state diagram:						
Result	Gas A flows	Gas B flows	Purge with Gas A	Purge with Gas B	Pump out flow module	Standby, vented, or EI mode
Control panel lights (LEDs)						
Gas A (green)	On	Off	On	Off	Off	Off
Gas B (amber)	Off	On	Off	On	Off	Off
Purge (red)	Off	Off	On	On	On	Off
Gas Off (red)	Off	Off	Off	Off	On	On
Valve state						
Valve A	Open	Closed	Open	Closed	Closed	Closed
Valve B	Closed	Open	Closed	Open	Closed	Closed
MFC	On → setpoint	On → setpoint	On → 100%	On → 100%	On → 100%	Off (→0%)
Isolation valve	Open	Open	Open	Open	Open	Closed

Pressure-related symptoms (overview)

The following symptoms are all related to high vacuum pressure. Each symptom is discussed in more detail in the following pages.

The mass flow controller is calibrated for methane, and the high vacuum gauge controller is calibrated for helium, so these measurements are not accurate in absolute terms, They are intended as a guide to typical observed readings. They were taken with the following set of conditions:

Source temperature	250°C
Quad temperature	106°C
Interface temperature	320°C
Helium carrier gas flow	1ml/min.

MFC (%)	Pressure (Torr)		
	Methane	**Isobutane**	**Ammonia**
10	5.6×10^{-5}	6.5×10^{-5}	4.7×10^{-5}
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20	9.8×10^{-5}	1.2×10^{-4}	8.5×10^{-5}
25	1.2×10^{-4}	1.4×10^{-4}	1.0×10^{-4}
30	1.4×10^{-4}	1.8×10^{-4}	1.2×10^{-4}
35	1.6×10^{-4}	2.0×10^{-4}	1.4×10^{-4}
40	1.8×10^{-4}	2.3×10^{-4}	1.6×10^{-4}
45	2.0×10^{-4}	2.6×10^{-4}	1.9×10^{-4}
50	2.2×10^{-4}	3.0×10^{-4}	2.1×10^{-4}
60	2.7×10^{-4}	3.5×10^{-4}	2.5×10^{-4}

Poor vacuum without reagent gas flow

Possible Cause Excess water in the background.

Action Scan from 10 – 40 amu. A large peak at *m/z* 19 (> *m/z* 17) indicates water in the background. If water is present, allow the instrument to bake out more and flow reagent gas through the lines to purge any accumulated water.

Possible Cause Air leak.

Action Run Methane Pre-tune. See page 54. A visible peak at *m/z* 32 indicates air in the system. Check for and correct any leaks. See the *Leaks* section at the beginning of this chapter.

Possible Cause The foreline pump is not working properly.

Action Replace the pump oil. If that does not help, it may be necessary to replace the pump. Contact your local Hewlett-Packard Customer Engineer.

Possible Cause The turbo pump is not working properly.

Action Check the pump speed. It should be at least 95%. Contact your local Hewlett-Packard service representative

CAUTION Use of ammonia as reagent gas can shorten the life of the foreline pump oil and possibly of the foreline pump itself. See the Maintenance chapter in this manual.

High pressure with reagent gas flow

Possible Cause The reagent gas flow rate is too high.

Action On the flow controller, turn down reagent gas flow as appropriate. Verify that reagent ion ratios are correct. See page 54.

Possible Cause Air leak.

Action Run Methane Pre-tune. See page 54. Visible peak at *m/z* 32 indicates air in the system. Check for and correct any leaks. See the *Leaks* section at the beginning of this chapter.

Possible Cause Interface tip seal wasn't installed.

Action Check the source storage box. If the seal is not in the box, vent the MSD and verify that the seal is correctly installed.

Pressure does not change when reagent flow is changed

Possible Cause The reagent gas regulator is closed.

Action Check and, if necessary, open the reagent gas regulator.

Possible Cause The reagent gas regulator is set to the wrong pressure.

Action Set the reagent gas regulator to 10 psi (70 kPa) for methane or to 3 – 10 psi (20 – 70 kPa) for isobutane or ammonia.

Possible Cause The valve on the reagent gas bottle is closed.

Action Check and, if necessary, open the valve on the reagent gas bottle.

Possible Cause The reagent gas supply is empty.

Action Check, and if necessary, replace the reagent gas supply.

Possible Cause Reagent lines kinked, bent, pinched, or disconnected.

Action Inspect the reagent lines and repair any defects. Check especially to make sure the reagent line is connected to the tee connector on the end of the GC interface.

Possible Cause GC/MSD interface clogged or damaged.

Action Check for flow and repair or replace components as indicated.

Signal-related symptoms (overview)

This section describes symptoms related to the signal. The symptom may be too much signal, too little signal, a noisy signal, or an incorrect signal. Signal-related symptoms are generally observed during tuning but may also be observed during data acquisition.

Error messages in autotune due to insufficient signal may vary.

The following symptoms are covered in more detail in this section:

- No or low reagent gas signal. See page 81.
- No or low PFDTD signal. See page 83.
- Excessive noise. See page 84.
- Low chromatographic signal abundance. See page 84.
- Low signal-to-noise ratio.
- Large peak at *m/z* 19. See page 85.
- Peak at *m/z* 32. See page 86.

No peaks

When troubleshooting “no peaks” it is important to specify what mode of operation is being used, and what kind of peaks are not being seen. Always start with methane PCI and verify presence of reagent ions.

No reagent gas peaks in PCI

If MSD has been working well and nothing seems to have been changed

- Wrong tune file loaded, or tune file corrupted
- Wrong ion polarity (there are no reagent ions visible in NCI)
- No reagent gas flow; look for background ions and check pressure
- Wrong reagent gas selected for the tune file (looking for wrong ions)
- Large air leak
- Dirty ion source
- Poor vacuum (pump problem). See page 74.

If MSD was recently switched from EI to CI

- Interface tip seal not installed
- No reagent gas flow
- Analyzer not sealed (big air leak)
- Wrong tune file loaded or tune file corrupted
- Ion source not assembled or connected correctly
- Wrong reagent gas selected for the tune file (looking for wrong ions)

No PFDTD peaks in PCI

- Incorrect reagent gas. There ***are*** no PCI PFDTD peaks created with isobutane or ammonia. Switch to methane.
- Analyzer not sealed (big air leak)
- No calibrant in vial
- Defective calibration valve
- Air leak in carrier or reagent gas path

No reagent gas peaks in NCI

- Reagent gases do not ionize in NCI; look for background ions instead.
- Verify tune parameters
- If no background ions are visible, go back to methane PCI

No PFDTD calibrant peaks in NCI

- Look for background ions
- Verify tune parameters
- Go back to methane PCI

No sample peaks in NCI

- Look for background ions
- Go back to methane PCI

Large peak at *m/z* 283 in NCI OFN spectrum

- Look for background ions
- Find and fix your small air leak

No or low reagent gas signal

Possible Cause If you have just installed the CI ion source, and have an air leak or large amounts of water in the system, and have run one or more autotunes, the ion source is probably dirty now.

Action Fix the air leak.
Clean the ion source. Then bake out for 8 hours before tuning. See the *Maintenance* chapter in this manual for more information.

Possible Cause The wrong reagent gas is flowing.

Action Turn on the correct reagent gas for your tune file.

Possible Cause Ion polarity is set to **Negative**. No reagent gas ions are formed in NCI.

Action Switch to **Positive** ionization mode.

Possible Cause The reagent gas flow is set too low.

Action Increase the reagent gas flow.

Possible Cause Reagent gas supply tubing is blocked, kinked, pinched, or disconnected.

Action Inspect and, if necessary, repair or replace the reagent gas supply tubing.

Possible Cause Wrong filament wires are connected to filament.

Action Make sure that the filament 1 wires are connected to the CI ion source filament and that the filament 2 wires are connected to the dummy filament.

Possible Cause Carbon has built up on the filament, or filament has sagged out of alignment.

Action Inspect the filament. If necessary, replace the filament.

Possible Cause Too much air or water in the system.

Action Run the methane pre-tune. Peaks at *m/z* 32 and 19 usually indicate air and water, respectively. Bake out and purge the instrument until the peak at *m/z* 32 is smaller than that at *m/z* 31 and the peak at *m/z* 19 is reduced to a very low level. If the peak at *m/z* 32 does not decrease, an air leak is likely. See the *Leaks* section at the end of this chapter for more information.

Possible Cause The signal cable is not connected.

Action Check and, if necessary, reconnect the signal cable.

Possible Cause The filament or filament support is shorted to the ion source body or repeller.

Action Inspect the filament. If necessary, realign the filament support arms.

Possible Cause The electron inlet hole is blocked.

Action Inspect the electron inlet hole. If necessary, clean the hole with the supplied 0.016-inch drill bit. If the electron inlet hole is that dirty, the entire ion source probably needs to be cleaned. See the *Maintenance* chapter in this manual for more information.

Possible Cause Ion source wires are not connected, or incorrectly connected.

Action Inspect the repeller. Make sure the repeller lead is firmly attached to the repeller. Inspect the wires to the ion focus and entrance lenses. If the connections are reversed, correct the problem.

Possible Cause One of the electron multiplier leads (in the vacuum manifold) is not connected.

Action Check and, if necessary, reconnect the electron multiplier leads.

Possible Cause Saturated methane / isobutane gas purifier.

Action Replace the gas purifier.

No or low PFDTD signal, but reagent ions are normal

Possible Cause You are flowing any reagent gas but methane in PCI.

Action Switch to methane.

Possible Cause Wrong or corrupted tune file loaded.

Action Check your tune file.

Possible Cause No PFDTD in the calibrant vial.

Action Inspect the calibration vial on the back of the flow controller. If necessary, fill the vial with PFDTD. Do not fill the vial completely; keep the level at least 0.5 cm from the top of the vial.

Possible Cause The pressure of the methane entering the flow controller is too high.

Action Make sure the regulator on the methane supply is set to 10 psig (70 kPa).

Possible Cause The CI ion source is dirty.

Action Clean the ion source. See the *Maintenance* chapter in this manual for more information.

Possible Cause The calibration valve was not purged after the vial was refilled.

Action Purge the calibration valve as described in the *Maintenance* chapter. Then clean the ion source.

Possible Cause The calibrant vial was overfilled. Excess PFDTD can quench the chemical ionization reactions.

Action Check the level of the PFDTD in the calibration vial as described in *Maintenance* chapter.

Excessive noise or low signal-to-noise ratio

Possible Cause The GC injection port needs maintenance.

Action Refer to the HP 6890 GC manual.

Possible Cause The CI ion source is dirty.

Action Clean the ion source. See the *Maintenance* chapter in this manual for more information.

Possible Cause Poor vacuum

Action Check the pressure on the high vacuum gauge controller.

Possible Cause Air leak.

Action Run Methane Pre-tune (in PCI). Large peak at *m/z* 32 indicates air in the system. Check for and correct any leaks. See the *Leaks* section at the beginning of this chapter.

Possible Cause Saturated methane / isobutane gas purifier.

Action Replace the gas purifier.

Large peak at *m/z* 19

If the abundance of the peak at *m/z* 19 is more than twice the abundance of the peak at *m/z* 17, then there is probably too much water in the system.

Possible Cause The system was not baked out sufficiently after it was last vented.

Action Bake out the system as described in the *Maintenance* chapter of this manual.

Possible Cause Moisture left over in the reagent gas supply tubing and flow module.

Action Purge the reagent gas supply lines for at least 60 minutes. See the *Maintenance* chapter.

Possible Cause Contaminated reagent gas supply.

Action Replace the reagent gas supply and purge the lines and flow module.

Possible Cause Saturated methane / isobutane gas purifier.

Action Replace the gas purifier.

Peak at *m/z* 32

A visible peak at *m/z* 32 in methane pre-tune often indicates air in the system.

Possible Cause Residual air from recent venting — check for water indicated by a large peak at *m/z* 19.

Action Bake out the system as described in the *Maintenance* chapter of this manual.

Possible Cause New or dirty reagent gas supply tubing.

Action Purge the reagent gas supply lines and flow module *for at least 60 minutes* as described in the *Maintenance* chapter of this manual.

Possible Cause Air leak.

Action Check for leaks and correct any that you find. See the *Leaks* section at the end of this chapter for more information. After all leaks have been corrected, clean the ion source.

Possible Cause Contaminated reagent gas supply. Suspect this if you have recently replaced your gas tank, and you have ruled out air leaks.

Action Replace the reagent gas supply.

Possible Cause The capillary column is broken or disconnected.

Action Inspect the capillary column. Make sure it is not broken and it is installed correctly.

Possible Cause Saturated methane / isobutane gas purifier.

Action Replace the gas purifier.

Tuning-related symptoms (overview)

This section describes symptoms related to tuning. Most symptoms involve difficulties with tuning or with the results of tuning. The following symptoms are covered in this section:

- CI ion ratio is difficult to adjust or unstable
- High electron multiplier voltage
- Can not complete autotune
- Peak widths are unstable
- Split peaks during autotune
- Incorrect *m/z* 70 abundance in tune report

Reagent gas ion ratio is difficult to adjust or unstable

Possible Cause Residual air and water in the MSD or in the reagent gas supply lines.

Action Run the methane pre-tune. Air will appear as a peak at *m/z* 32 and excessive water as a peak at *m/z* 19 > *m/z* 17. If either of conditions is present, purge the reagent gas supply lines and bake out the MSD. See page 40. Continued presence of a large peak at *m/z* 32 may indicate an air leak. After correcting the problems, you may need to clean the ion source.

Possible Cause Air leak.

Action Run Methane Pre-tune (in PCI). Large peak at *m/z* 32 indicates air in the system. Check for and correct any leaks. See the *Leaks* section at the beginning of this chapter.

Possible Cause The reagent gas supply is at the wrong pressure.

Action Check the regulator on the reagent gas supply. It should be adjusted to 20 psi (140 kPa).

Possible Cause A leak in the reagent gas delivery path. This is especially likely if you have set the methane flow much higher than normal and the ratio is still too low.

Action Check the reagent gas path. Tighten fittings.

Possible Cause The CI ion source is dirty.

Action Clean the ion source. See the *Maintenance* chapter of this manual for more information.

Possible Cause The interface tip seal is incorrectly placed, damaged, or missing.

Action Inspect the interface tip seal. If necessary, remove and reinstall it to insure a good seal with the CI ion source. Replace it if it is damaged. Install it if it is missing.

High electron multiplier voltage

The electron multiplier voltage can range from a few hundred volts to 3000 V. If the CI autotune program consistently sets the electron multiplier voltage at or near 3000 V, but can still find peaks and complete the tune, it may indicate a problem.

Possible Cause The filament is worn out. The CI filament may wear out without actually breaking. Check the Electron Energy ramp; the curve should have a definite maximum with an inflection point. If the curve is linear with a positive slope and no inflection point, and the EMV is high, the filament has stretched to the point where it does not line up with the hole in the ion source body, and most electrons are not getting into the source.

Action Replace the filament.

Possible Cause The analyzer is not at the proper operating temperature.

Action Verify the ion source and quadrupole temperatures. The default source temperature is 250°C for PCI and 150°C for NCI. The quadrupole temperature is 106°C for both CI modes.

Possible Cause The CI ion source is dirty.

Action Clean the ion source. See the *Maintenance* chapter in this manual for more information.

Possible Cause The electron multiplier (detector) is failing. Switch to EI mode and confirm.

Action Replace the electron multiplier.

Can not complete autotune

Possible Cause Wrong or corrupted tune file.

Action Check the tune parameters.

Possible Cause The *m/z* 28/27 ion ratio (for methane) is incorrect. The correct ratio should be between 1.5 and 5.0.

Action If the ion ratio is incorrect, adjust it. See page 54.

Possible Cause The CI ion source is dirty.

Action Clean the ion source. See the *Maintenance* chapter in this manual for more information.

Possible Cause Too much air or water in the system.

Action See the *Leaks* section of this chapter for more information. After eliminating these problems, clean the ion source.

Peak widths are unstable

Possible Cause Wrong or corrupted tune file.

Action Check the tune parameters.

Possible Cause The CI ion source is dirty.

Action Clean the ion source. See the *Maintenance* chapter of this manual for more information.

Possible Cause Air leak.

Action Run Methane Pre-tune (in PCI). A visible peak at *m/z* 32 indicates air in the system. Check for and correct any leaks. See the *Leaks* section at the beginning of this chapter. After eliminating all air leaks, clean the ion source.

7

Maintenance

Maintenance

This chapter describes maintenance procedures and requirements that are unique to HP 5973 MSDs equipped with the Chemical Ionization hardware. Maintenance information in the *HP 5973 MSD Hardware Manual* still applies to MSDs equipped with the CI unless it is superseded by information in this chapter. Be sure to read *Before starting* in the chapter *Maintaining the MSD* of the *HP 5973 MSD Hardware Manual* (G1099-90001) before using any of the procedures or information in this chapter.

Maintenance videos on Reference Collection CD-ROM

Most of these maintenance procedures are demonstrated on the multimedia MSD Reference Collection CD-ROM. Please view these videos.

CI increases the need for ion source cleaning

The primary effect of operating the MSD in CI mode is the need for more frequent ion source cleaning. In CI operation, the ion source chamber is subject to more rapid contamination than in EI operation because of the higher source pressures required for CI.

WARNING **Always perform any maintenance procedures using hazardous solvents under a fume hood. Be sure to operate the MSD in a well-vented room.**

Ammonia CI increases the need for foreline pump maintenance

Ammonia, when used as a reagent gas, it will also change the maintenance requirements slightly. Ammonia causes the foreline pump oil to break down more quickly. Therefore, the oil in the foreline vacuum pump must be checked and replaced more frequently.

Always purge the MSD with methane after flowing ammonia.

Be sure to install the ammonia so the tank is in an upright position. This will help prevent liquid ammonia from getting into the flow module.

To clean the CI ion source

The CI ion source has slightly different cleaning requirements than the standard EI ion source. See the procedure in the HP 5973 MSD Reference Collection CD-ROM.

Frequency of cleaning

Because the CI ion source operates at much higher pressures than the EI ion source, it will probably require more frequent cleaning than the EI ion source. Cleaning of the source is not a scheduled, periodic maintenance procedure. The source should be cleaned whenever there are performance anomalies that are associated with a dirty ion source. See the *Troubleshooting* chapter for symptoms that indicate a dirty ion source. ***Visual appearance is not an accurate guide to cleanliness of the CI ion source. The CI ion source can show little or no discoloration yet still need cleaning.*** Let analytical performance be your guide.

Cleaning procedure

Cleaning the CI ion source is very similar to cleaning the EI ion source. Use the cleaning procedure in the chapter *Maintaining the MSD* of the *HP 5973 MSD Hardware Manual* with the following exceptions:

- The CI ion source may not look dirty but deposits left by chemical ionization are very difficult to remove. Clean the CI ion source thoroughly.
- Use a round wooden toothpick to gently clean out the electron entrance hole in the source body and the ion exit hole in the drawout plate.
- Do not use halogenated solvents, and use hexane for the final rinse.

NOTE

The HP 5973 MSD Reference Collection CD-ROM illustrates using a small drill bit to clean the small holes in the ion source body and drawout plate. This is not recommended. Use the tip of a clean, round toothpick instead.

See Also

Refer to the MSD Reference Collection CD-ROM for video demonstrations of ion source cleaning and other maintenance procedures.

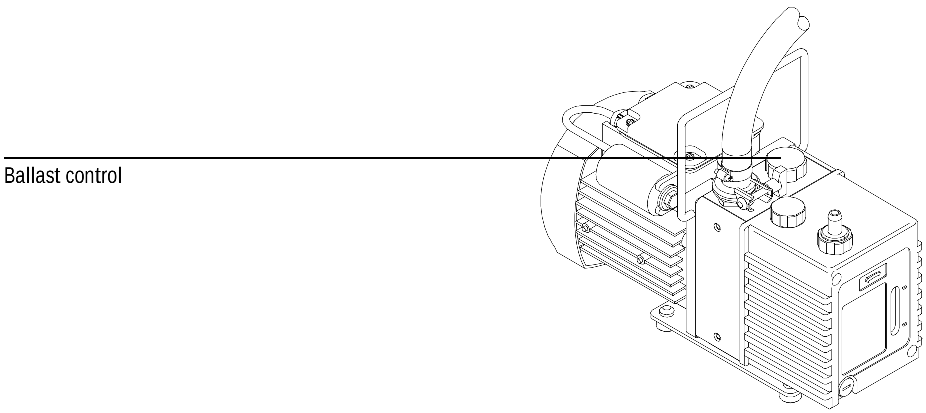
CAUTION

Do not use any halogenated solvents to clean the CI ion source.

To minimize foreline pump damage from ammonia

Gas ballasting for an hour every day removes most, of the ammonia from the pump oil. This will greatly increase the life of the pump.

CAUTION Only perform this procedure if the pump is at normal operating temperature. The water in the air can cause condensation of the ammonia at the ballast valve if the pump is cold.



1 **Open the ballast valve on the foreline pump all the way (several turns counterclockwise)**

2 **The sound of the pump will get much louder.**

3 **Leave the ballast valve open for one hour.**

You can continue to run samples while the pump is ballasting.

4 **Close the ballast valve.**

Leaving the ballast valve open all the time will result in loss of pump oil and damage to the pump.

CAUTION Always purge the flow module with methane after flowing ammonia.
The use of ammonia reagent gas also requires that the foreline pump oil be changed every 2–3 months instead of the usual six months.

To replace the methane/isobutane gas purifier

Materials needed:

Methane/isobutane gas purifier (G1999-80410)
Front ferrule for 1/8-inch tubing (5180-4110)
Rear ferrule for 1/8-inch tubing (5180-4116)
Tubing cutter (8710-1709)

The methane/isobutane gas purifier needs to be replaced after four tanks of reagent gas. This frequency may vary depending on purity of the gas and care taken in uncapping and installing the gas purifier. A large leak upstream from the gas purifier can quickly exhaust the reduced metal of its oxygen and moisture traps.

1 **To install the methane/isobutane gas purifier, follow the instructions on the label for installation and replacement intervals.**

CAUTION Be sure not to remove the caps until you are ready to install the gas purifier. Only remove the caps in the gas flow to prevent contamination by air.

WARNING **Methane is flammable. Extinguish all flames in the area before turning on gas flow.**

2 **Disconnect the fittings on the old filter.**

3 **Remove the ferrules from the tubing at the outlet of the gas purifier.**

Using the tubing cutter, cut off the end of the tubing with the ferrules.

4 **Install the new filter.**

5 **Purge the new filter.**

6 **Cap the old filter and prepare it to be sent for regeneration.**

See the instructions on the label.

To refill the CI calibrant vial

Materials needed: PFDTD calibrant (8500-8130)

1 **Set the reagent gas flow to Gas Off**

2 **Vent the MSD**

3 **Remove the capillary column from the GC/MSD interface**

4 **Pull the MSD away from the GC**

5 **Loosen the nut holding the vial in place**

6 **Remove the calibrant vial**

CAUTION Do ***not*** rinse the vial with any solvents. ***Never*** expose the inside of the vial to chlorinated solvents or isopropyl alcohol or water — this will result in severe loss of CI sensitivity.

7 **Fill the vial to within 0.5 cm of the top with fresh PFDTD calibrant (8500-8130).**

8 **Replace the vial and tighten the nut.**

9 **Reposition the MSD next to the GC.**

10 **Reinstall the capillary column.**

11 **Pump down the MSD. See page 40.**

12 **Purge the calibration valve. See page 99.**

CAUTION After removing the calibrant vial, you ***must*** purge the calibration valve. Failure to do so will result in severe contamination of the ion source and damage to the electron multiplier

To purge the CI calibration valve

After adding new PFDTD to the calibrant vial, you must purge the air out of the vial and valve.

1 **If the vacuum gauge controller is on, turn it off.**

2 **Turn on Gas A.**

3 **Turn on Purge.**

4 **In Diagnostics and Vacuum Control view, select Purge Cal Valve under the Vacuum menu.**

This will open the CI calibration valve for several minutes with all analyzer voltages turned off.

CAUTION

After removing the calibrant vial, you ***must*** purge the calibration valve. Failure to do so will result in severe contamination of the ion source and damage to the electron multiplier.

To connect the vacuum gauge controller

Materials needed:

Gauge controller (HP 59864B)
Triode gauge cable (8120-6573)

The high-vacuum gauge controller is required for operating the MSD in CI mode.

WARNING

Never connect or disconnect the cable from the triode gauge tube while the MSD is under vacuum. Risk of implosion and injury due to broken glass exists.

WARNING

Never connect or disconnect the cable from the triode gauge tube while the controller is turned on. Dangerous voltages are present on the cable.

CAUTION

Do ***not*** use an HP 59864***A*** (older model) triode gauge controller with the HP 5973 CI MSD.

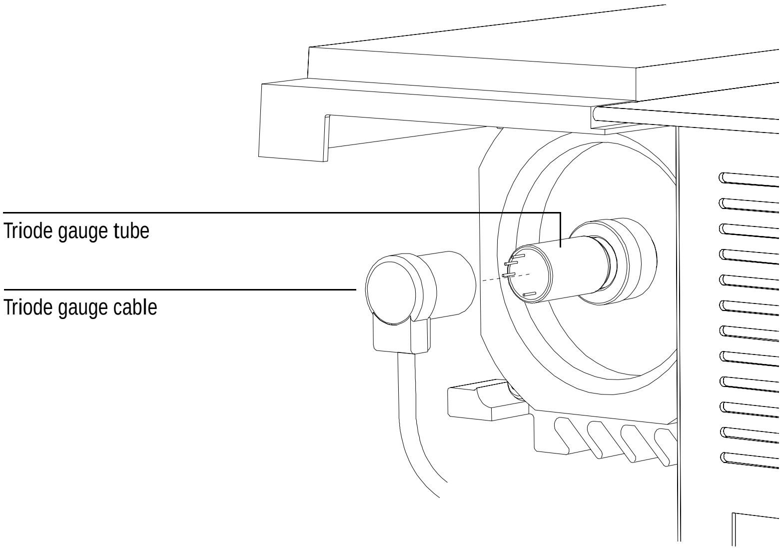
1 **Connect the triode gauge cable to the triode gauge tube.**

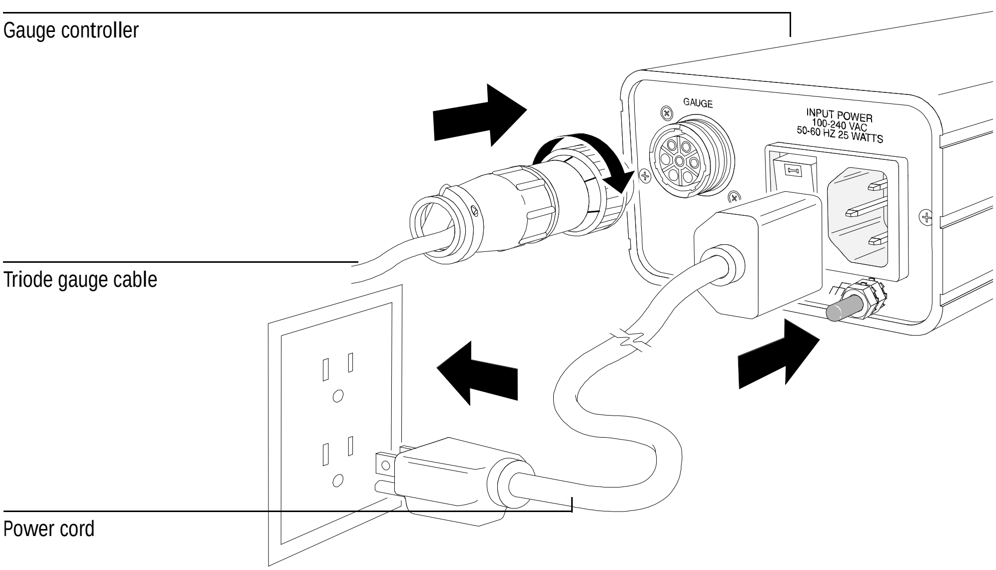
2 **Connect the other end of the triode gauge cable to the gauge controller.**

3 **Connect the power cord to the gauge controller.**

4 **Connect the other end of the power cord to an appropriate electrical outlet.**

5 **Pump down the MSD.**


Triode gauge tube
Triode gauge cable


Gauge controller
GAUGE
INPUT POWER
100-240 VAC
50-60 HZ 25 WATTS
Triode gauge cable
Power cord

To clean the reagent gas supply lines (tubing)

Materials needed:

Clean, dry nitrogen
Heat gun
Tubing cutter (8710-1709)

If the reagent gas lines become contaminated, they can be cleaned.

1 **Disconnect the reagent gas tubing from the gas supply, the gas purifier, and the MSD.**

2 **Cap the gas purifier following the instructions on the label.**

3 **Connect one end of the tubing to a supply of clean, dry nitrogen and turn on gas flow.**

4 **Use the heat gun to warm the tubing, starting at the supply end and working your way to the free end.**

5 **Repeat for any other pieces of tubing that need to be cleaned.**

6 **Reconnect the tubing to the gas supply, gas purifier, and MSD.**
Follow the instructions on the gas purifier label.

WARNING **Do not heat the gas tubing when reagent gas is flowing.**

CAUTION Do not put liquids into the tubing. Do not heat the tubing when it is connected to the MSD.

8

Parts

Parts

This chapter lists parts that may be required to maintain the HP 5973 MSD with CI. The parts listed in this chapter are related directly to the accessory; other parts for the MSD can be found in the *Parts* chapter of the HP 5973 MSD Hardware Manual.

To order parts

To obtain parts for the HP 5973 MSD, address the order or inquiry to your local Hewlett-Packard office. Supply them with the following information:

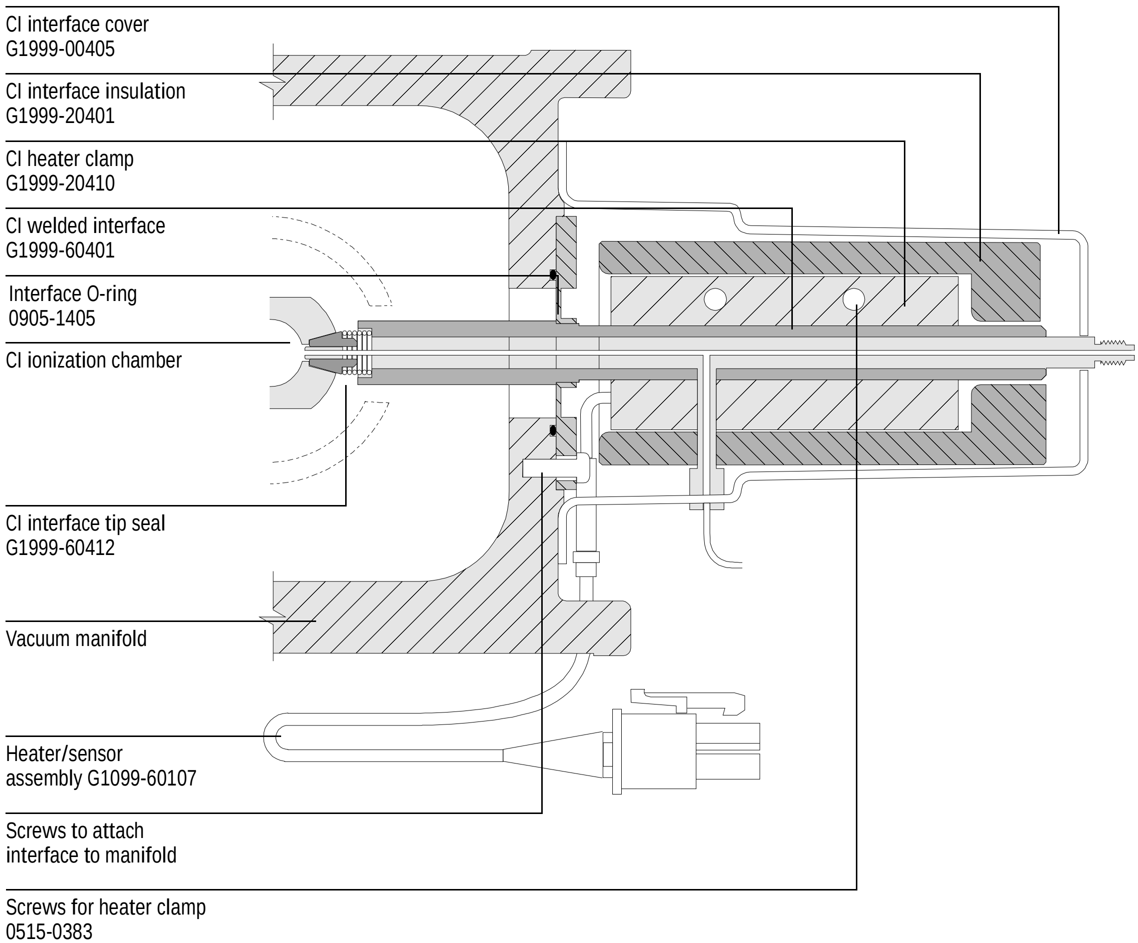
- Model and serial number of your MSD
- Serial number of your CI flow module
- HP part number(s) of the part(s) needed
- Quantity of each part needed

If you cannot find a part you need

If you need a part that is not listed in this chapter, check the Hewlett-Packard Analytical Supplies Catalog or the on-line catalogue on the worldwide web at **<http://www.dmo.hp.com/cagcat/pub/HOME.htm>**. If you still cannot find it, contact your Hewlett-Packard service representative or your Hewlett-Packard office.

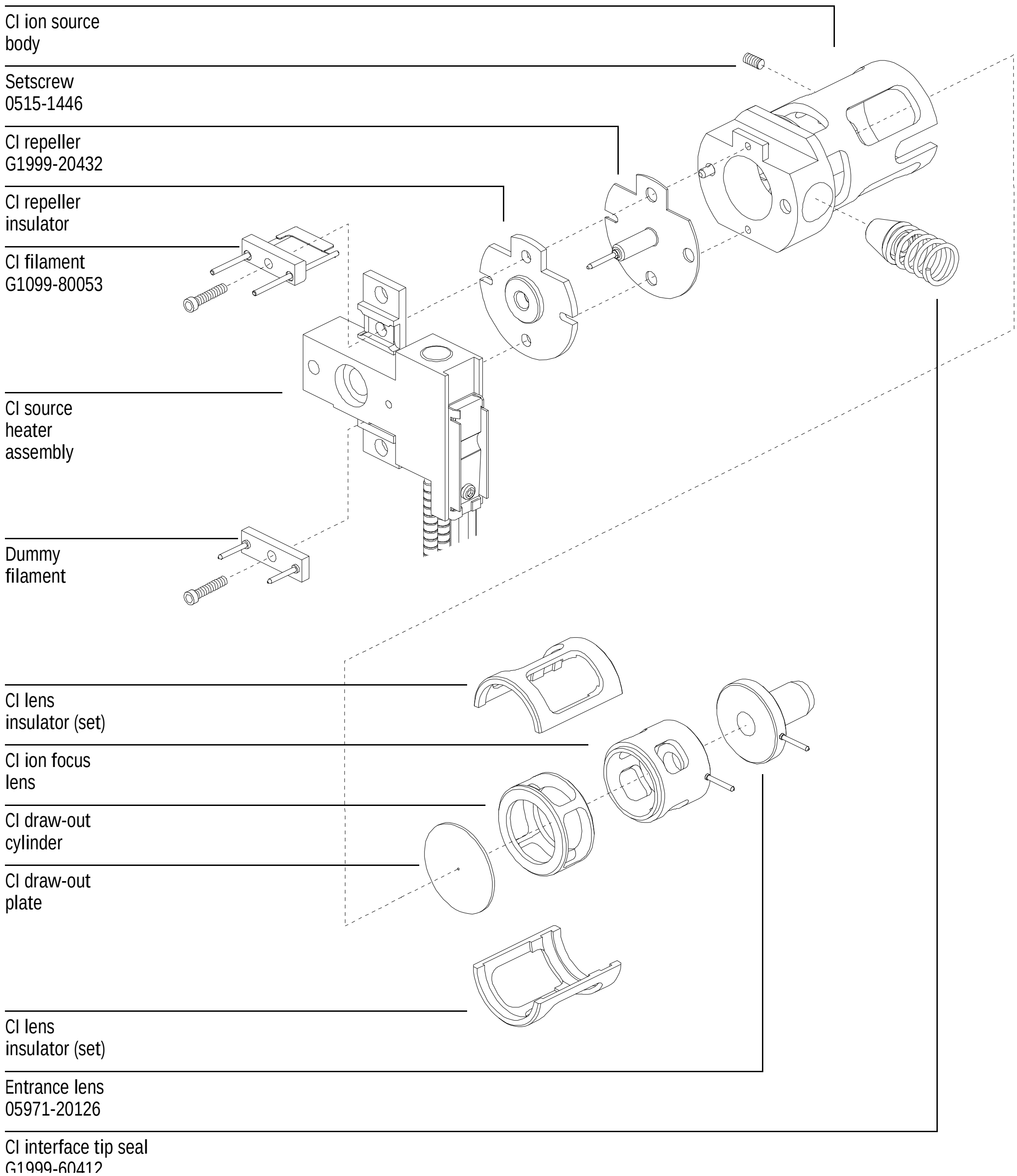
GC/MSD interface parts

Description	HP part number
CI/EI GC/MSD interface assembly	G1999-60400
Heater clamp	G1999-20410
Heater/sensor assembly	G1099-60107
Interface cover	G1999-00405
Interface insulation (two pieces)	G1999-20401
Screws for heater clamp	0515-0383
Screws to attach interface to manifold	0515-0380
Welded interface	G1999-60401
Interface tip seal	G1999-60412
Vespel blank	5181-3308


CI interface cover
G1999-00405
CI interface insulation
G1999-20401
CI heater clamp
G1999-20410
CI welded interface
G1999-60401
Interface O-ring
0905-1405
CI ionization chamber
CI interface tip seal
G1999-60412
Vacuum manifold
Heater/sensor
assembly G1099-60107
Screws to attach
interface to manifold
Screws for heater clamp
0515-0383

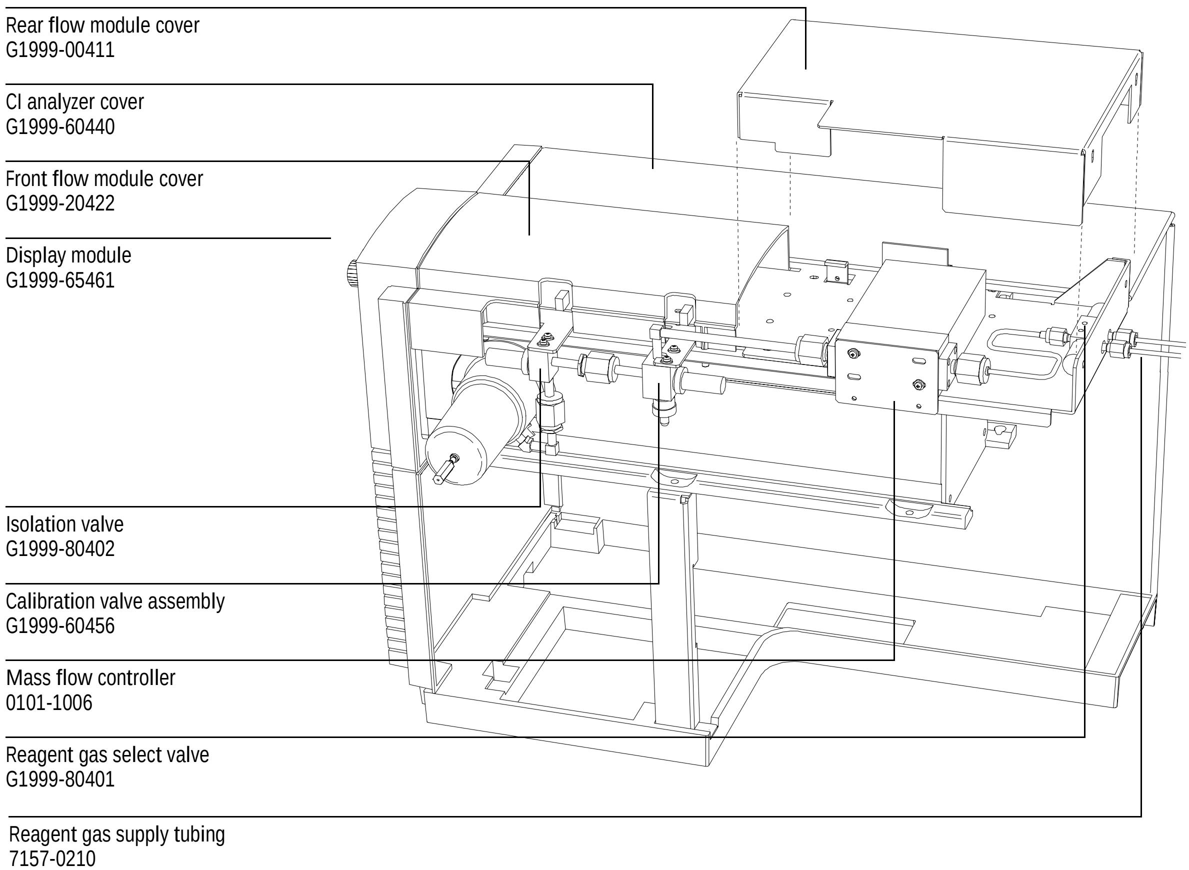
CI ion source parts

Description	HP part number
Box for ion source shipping and storage	G1999-65001
CI ion source (tested)	G1999-65402
CI drawout cylinder	G1999-20444
CI drawout plate	G1999-20446
CI filament	G1099-80053
CI heater block	G1999-20431
CI interface tip seal	G1999-60412
CI ion focus lens	G1999-20443
CI lens insulators (set)	G1999-20445
CI repeller	G1999-20432
CI repeller insulator	G1999-20433
CI source body	G1999-20430
CI source heater assembly	G1999-60414
Dummy filament	G1999-60454
Entrance lens	05971-20126
Screw, skt-hd cap for mounting filaments	G1999-20021
Setscrew for mounting heater and lens stack	G1999-20021
Screw, M3 X 4L socket head for mounting RTD	0515-2903
Screw, M2 × 8L mounts source to radiator	0515-1046


CI ion source body
Setscrew 0515-1446
CI repeller G1999-20432
CI repeller insulator
CI filament G1099-80053
CI source heater assembly
Dummy filament
CI lens insulator (set)
CI ion focus lens
CI draw-out cylinder
CI draw-out plate
CI lens insulator (set)
Entrance lens 05971-20126
CI interface tip seal G1999-60412

Flow control module parts

Description	HP part number
CI flow control module (complete)	G1999-65450
Calibration valve assembly	G1999-60456
PFDTD calibrant	8500-8130
Sample vial	05980-20018
Sample vial O-ring, 1/4-inch Viton	0905-1217
Solenoid valve and cable	G1999-80405
CI main power harness cable	G1999-60462
Display module	G1999-65461
Flow control knob	0370-3401
Flow control PCA	G1999-65005
Mass flow controller	0101-1006
Isolation valve	G1999-80402
Mass flow controller cable	G1999-60464
Reagent gas select valve	G1999-80401
VCR gasket, 1/4-inch, with retainer, one use only	0100-1436
VCR gasket, 1/8-inch, one use only	0100-0468
CI analyzer cover	G1999-60440
Front flow module cover	G1999-20422
Methane/isobutane gas purifier	G1999-80410
Reagent gas supply tubing, stainless steel, 1/8-inch	7157-0210
Rear flow module cover	G1999-00411
Swagelok fittings for gas purifier and inlet to flow module	
Ferrule, front, for 1/8-inch tubing, 20/package	5180-4110
Ferrule, rear, for 1/8-inch tubing, 20/package	5180-4116
Nut, for 1/8-inch tubing, 20/package	5080-8751
Nut and both front and rear ferrules, 20 sets/package	5080-8751


Rear flow module cover
G1999-00411
CI analyzer cover
G1999-60440
Front flow module cover
G1999-20422
Display module
G1999-65461
Isolation valve
G1999-80402
Calibration valve assembly
G1999-60456
Mass flow controller
0101-1006
Reagent gas select valve
G1999-80401
Reagent gas supply tubing
7157-0210

Ferrules

Description	HP part number
Blank, graphite-vespel	5181-3308
GC/MSD interface	
0.3-mm id, 85% Vespel 15% graphite, for 0.10-mm id columns	5062-3507
0.4-mm id, 85% Vespel 15% graphite, for 0.20-mm id and 0.25-mm id columns	5062-3508
0.5-mm id, 85% Vespel 15% graphite, for 0.32-mm id columns	5062-3506
0.8-mm id, 85% Vespel 15% graphite, for 0.53-mm id columns	5062-3538
Injection port	
0.27-mm id, 90% Vespel 10% graphite, for 0.10-mm id columns	5062-3518
0.37-mm id, 90% Vespel 10% graphite, for 0.20-mm id columns	5062-3516
0.40-mm id, 90% Vespel 10% graphite, for 0.25-mm id columns	5181-3323
0.47-mm id, 90% Vespel 10% graphite, for 0.32-mm id columns	5062-3514
0.74-mm id, 90% Vespel 10% graphite, for 0.53-mm id columns	5062-3512

Miscellaneous parts

Description	HP part number
Benzophenone, 100 pg/µl	8500-5440
Bipolar HED power supply	G1099-80018
Cotton swabs (100)	5880-5400
Foreline pump secondary containment tray	G1099-00015
Gloves, clean	
large	8650-0030
small	8650-0029
Methane/isobutane gas purifier	G1999-80410
OFN, 1 pg/µl	8500-5441
PFDTD calibrant	8500-8130
Powder, alumina	8660-0791
Reagent gas line, 20-ft 1/8” ID stainless steel, cleaned	7157-0210
Wipes, industrial, 300/package	9310-4828
Swagelok fittings for gas purifier and inlet to flow module	
Ferrule, front, for 1/8-inch tubing, 20/package	5180-4110
Ferrule, rear, for 1/8-inch tubing, 20/package	5180-4116
Nut, for 1/8-inch tubing, 20/package	5080-8751
Nut and both front and rear ferrules, 20 sets/package	5080-8751
Tubing cutter for stainless steel tubing	8710-1709
Tubing cutter replacement blades	8710-1710

Index

R

S

Safety Information – *Continued*

Electrical Safety

WARNING
Connecting the MSD to power sources which are not equipped with protective earth contacts creates a shock hazard for the operator and can damage the instrument.

Interrupting the protective conductor inside or outside the MSD or disconnecting the protective earth terminal creates a shock hazard for the operator and can damage the instrument.

Make sure the power cords supplied with the MSD are appropriate for your country and site before using them. Maintain easy access to the power cords so they can be disconnected during maintenance.

WARNING
The use of incorrect or makeshift fuses or the short-circuiting of fuse holders creates a shock hazard for the operator and can damage the instrument. Replace fuses only with fuses of identical current rating and type.

WARNING
Dangerous voltages are present inside the MSD even if the power switches are off. Turn off the MSD power switches and disconnect the MSD power cords from their outlets before removing any covers unless you are specifically instructed to do otherwise by this manual.

WARNING
Excessive fluctuations in the line voltage can create a shock hazard and can damage the instrument. Make sure the supply voltage does not fluctuate more than +5% or -10% from the rated voltage. This equipment must be installed in a Category II environment as defined in IEC664.

Thermal Safety

WARNING
Many parts of the MSD operate at dangerously high temperatures. Make sure the MSD is off and these parts are cool before removing any covers unless you are specifically instructed to do otherwise by this manual.

Chemical Safety

WARNING
The foreline pump exhaust and split vent exhaust will contain traces of the chemicals you are analyzing, as well as carrier and reagent gases. These could potentially be toxic. Vent the foreline pump exhaust and split vent exhaust outside your laboratory or into a fume hood. Be sure to comply with all local environmental regulations.

Hydrogen carrier gas is extremely flammable. Explosions can result if hydrogen is allowed to build up in the MSD or GC oven. Study the Hydrogen Carrier Gas Safety Guide (HP Part No. 5955-5398) before operating the MSD with hydrogen carrier gas.

CI reagent gases may be flammable and/or toxic. Practice appropriate safety precautions when using and handling these gases.

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