Introduction to Low Mass Range Electrostatic Ion Trap Mass Spectrometer

Technical Note

Introduction

Mass spectrometry (MS) is an analytical technique widely used to determine the molecular mass of individual and/or unknown compounds, analyze the chemical composition of complex gas samples, perform structural analysis of individual or unknown chemicals, verify the identity and purity of known substances, and provide data on isotopic analysis. Mass spectrometry is widely recognized as a very powerful and valuable gas analysis technology with wide ranging applications in both research and industrial fields.

Mass spectrometers of small size and limited mass range are often called residual gas analyzers (RGA), or partial pressure transducers, and are based upon quadrupole mass spectrometry (QMS) designs. These measurement instruments have been used for over three decades for contamination monitoring and as vacuum diagnostic tools. Ideally, these partial pressure transducers can be thought of as an extension of the total pressure transducers with small size, low power and fast response times. However, the QMS partial pressure transducers are generally larger and higher power due to the high power RF systems that are required to operate a QMS transducer and the slow 1-2 second measurement times for the range of gases of interest. The Ion Trap Mass Spectrometer (ITMS) from Granville-Phillips offers the small size, low power and fast response times of a total pressure sensor while offering the same measurement accuracy and resolution of low mass range QMS systems.

The Granville-Phillips 1-300 amu sensor is comprised of a replaceable hot-filament ionization source assembly, the Ion Trap, and an Electron Multiplier detector that are housed in an UHV compatible envelope.

The 300 amu sensor is used with all of Granville-Phillips' Vacuum Quality Monitor (VQM) Controllers. The Series 830 VQM Controller uses the sensor to provide accurate gas analysis data from 1 to 135 amu; the Series 850 VQM Controller will provide accurate gas analysis data over the entire 1 to 300 amu range.

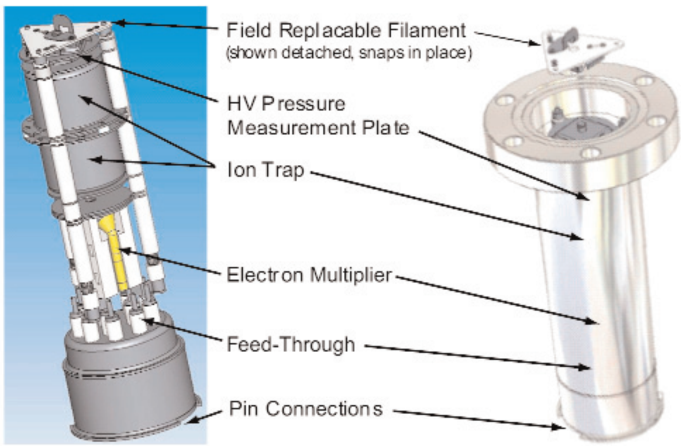
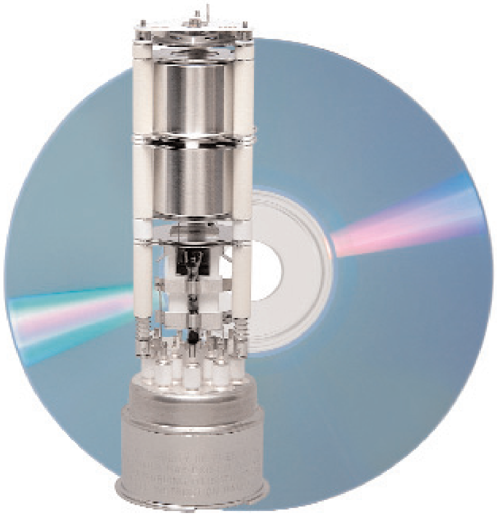


Figure 1: Ion Trap Mass Spectrometer Gauge



The Ion Trap Mass Spectrometer (ITMS)

The ITMS is a practical low-mass range electrostatic ion trap design that uses anharmonic resonant electrostatic trapping potentials as shown in the SIMION® simulation of Figure 2. The ITMS design is a simple electrostatic mirror structure of cylindrical symmetry with a center plate biased at a negative 1000 Vdc and located between two opposite grounded cup structures. The physical dimensions of the trap and the biasing structure create an electrostatic field as shown by the electrostatic equipotential lines. The typical flight paths of the ions within the trap are shown in Figure 2, where the amplitude of oscillation is less than the length of the trap. For clarity we have not shown the inlet and the outlet structures of the ITMS.

Ions stored inside the ion trap oscillate back-and-forth at a resonant frequency that is inversely proportional to the square root of their m/z. A convenient way to think of the oscillation and m/z relationship is to consider the interplay between the ion's potential and kinetic energies during an oscillation period. At the maximum amplitude point (farthest from the center) the ion's energy is 100% potential energy (PE) and is related to the distance to the center plate that is biased at a negative 1000 V (-1000 V). The PE is mass and charge independent and all ions within the trap, regardless of m/z, and have approximately the same PE.

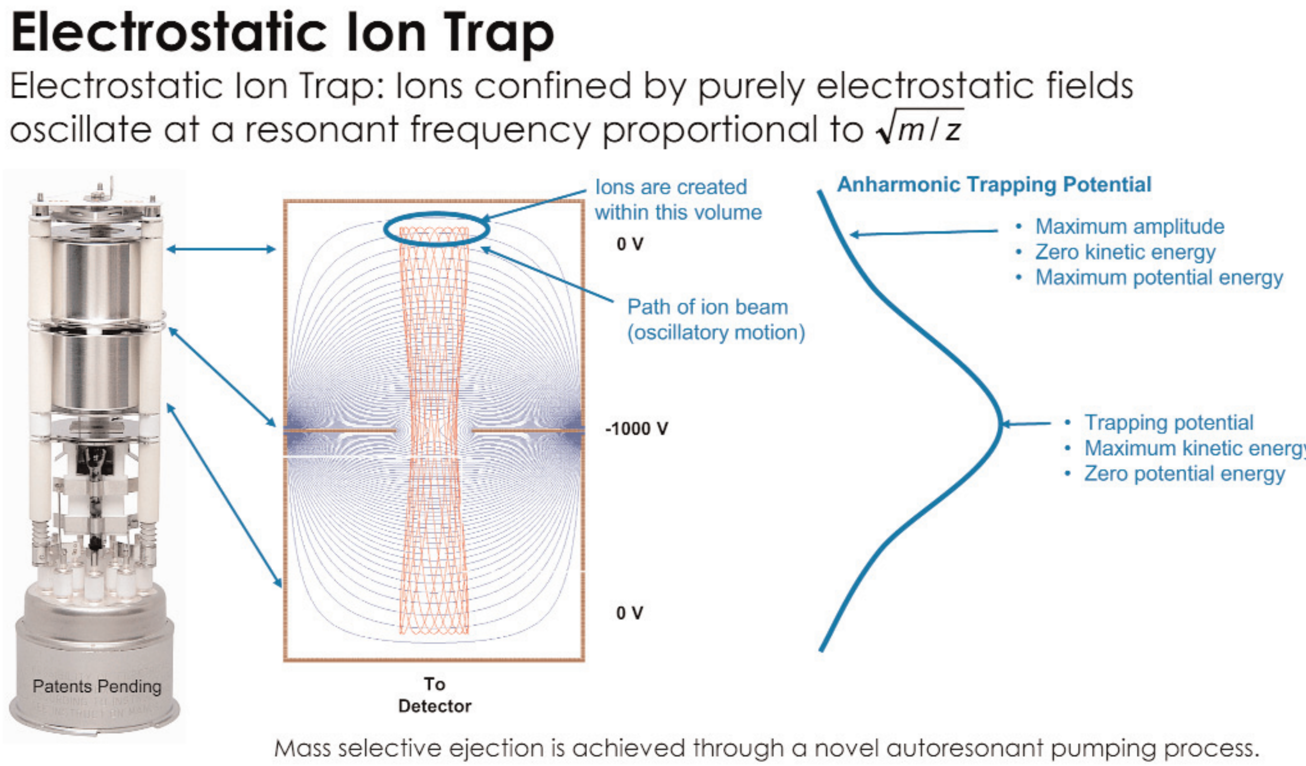


Figure 2: Electrostatic Ion Trap

When the ions are accelerated by the electrostatic field towards the center plate and reach the center plate aperture, their energy is now 100% kinetic energy (KE) and equal to $\frac{1}{2}mv^2$. Since all ions within the trap have the same KE that was equal to their initial PE, the velocity and oscillation frequency of the ions within the trap is then related to the $m/z^{1/2}$ and can be used for mass spectrometry. A novel methodology was developed to mass selectively increase the ion energy using low power RF signals until their oscillation amplitude exceeds the length of the trap where the ions can be detected.

The benefits of the ITMS design are:

Speed - 20x (or more) Faster than a QMS

Low Power - A Purely Electrostatic Device

Smaller Size / Reduced Surface Areas Reduce Outgassing

Excellent Performance at Low Masses (No Zero Blast)

Point Sample of Gas - Gas Ionization is Inside the Trap

Single Point Mass Calibration

Figure 3 shows the comparison between the Ion Trap (ITMS) and QMS performance. Two sets of device scans are shown, with the ITMS scans in blue and the QMS scans shown in red. Both top and bottom scan sets are over the same 1-100 amu mass (m/z) scan range and the measurements were at $1x10^{-7}$ Torr. The top scan set was run at 70ms, the time for the ITMS to complete a 1-100 amu scan. The bottom scan set was run at 1500ms, the time for the QMS to complete a 1-100 amu scan.

The ITMS scan in the top scan set (blue) shows low noise and good single-scan resolution. The range of commonly used gases from Argon (Ar, 40 amu), Water (H_2O, 18 amu), Carbon Dioxide (CO_2, 44 amu), and major Air Components Nitrogen (N_2, 28 amu) and Oxygen (O_2, 32 amu) at the appropriate 4/1 ratios are measured. Helium (He, 4 amu), a common leak detection gas, is properly measured. The QMS top scan (red) shows how much information you get from the QMS transducer in 70ms, where only Helium was detected and over represented (too large a peak) due to QMS zero blast issue.

The bottom scan of Figure 3 shows the 1500ms duration single scan QMS scan (red) with the measurement of the major Helium, Nitrogen, Oxygen, Argon and Carbon Dioxide peaks. Like in the top red QMS scan, the Helium peak is too high due to zero blast. The ITMS scan shows a noise reduced and highly defined measurement through the averaging of 21 scans during the same time period. The ITMS measurement also clearly shows Water and Freon peaks that were missed by the QMS.

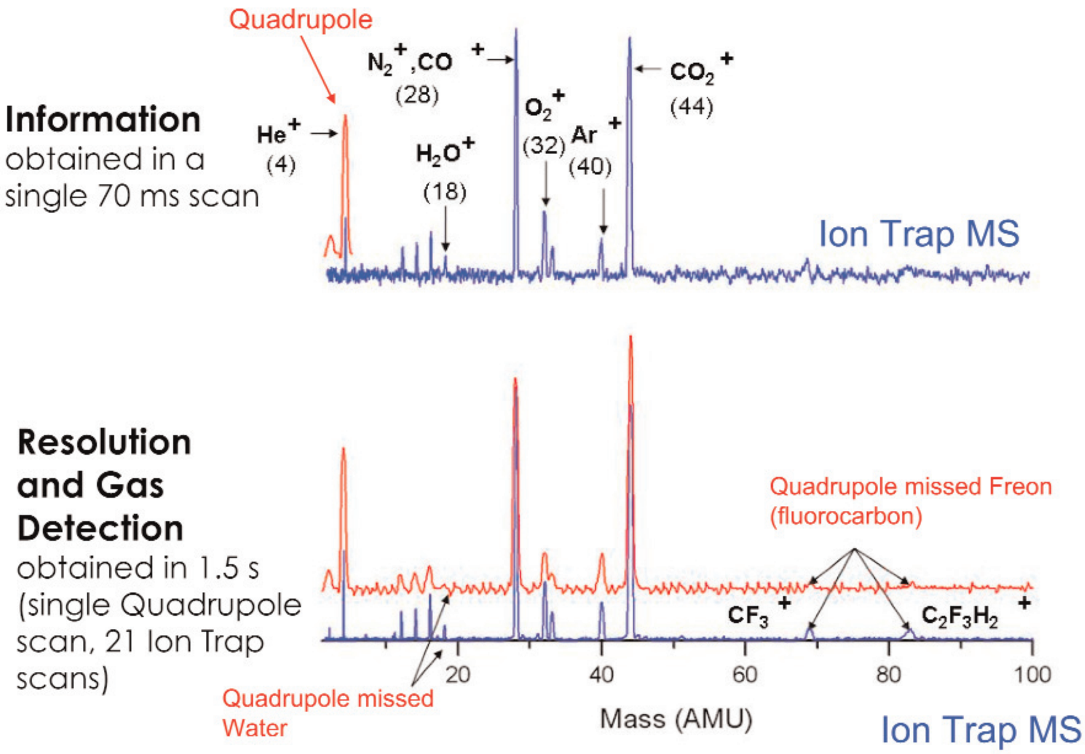


Figure 3: Ion Trap vs. Quadrupole

Figure 4 shows an ITMS 4ms single scan (not averaged) for detecting an air leak, where the scan range was limited from 26 amu to 34 amu. The combination of high sensitivity and high speeds makes the ITMS device the new standard for fast closed-loop process control based on compositional analysis.

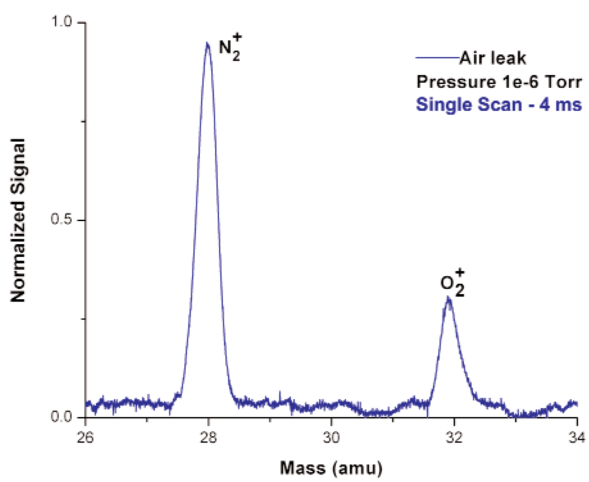


Figure 4: Fast Air Leak Detection

The ITMS is a purely electrostatic device, where electrostatic repulsion between ions in the oscillating beam leads to space charge limitations to the density of charge that can be stored in the ITMS device. This property is largely pressure independent and the amount of charge stored within the trap is relatively constant over its usable range, therefore the performance of the trap is more consistent over its usable range. Consequently, the speed and sensitivity advantage of the ITMS relative to a QMS increases with decreasing pressure, making the ITMS technology ideal for ultra high vacuum (UHV) applications. The 1-300 amu range ITMS device (electron source, Ion Trap and Detector) is about the same size as our Granville-Phillips® standard Stabil-Ion® total pressure ionization gauge (4 cm in diameter x 13 cm length). The small size of the ITMS device leads to less surface area exposed to vacuum, and minimized outgassing and processing effects compared to full range quadrupole devices.

Another characteristic of the ITMS fast scanning speed is that the sampled data better represents the gas components at the time of measurement if the gas components are rapidly changing. The fast scan rates provide a more accurate "point measurement" of the sample gas that enables the ITMS to better capture transient events, especially in the UHV pressure ranges.

Surface science and the detection of pressure bursts due to faulty vacuum valve operation are sample applications that can take advantage of the "point measurement" capabilities of an ITMS device.

The ITMS is intrinsically a ratiometric device. Because the ITMS stores a fixed amount charge, the gas component partial pressures represent a portion of the 100% of the total charge in the ion trap. In many applications where concentrations need to be tracked and reported, ratiometric information is preferred over absolute partial pressure information and is a native output of the ITMS device. Where absolute partial pressure information is needed, the output of the ITMS can be easily scaled using independent total pressure information to provide partial pressure outputs. In addition, the ratiometric output makes the ITMS much less sensitive to detector aging effects that are common in QMS detectors.

Most QMS systems provide mass range specifications which start at or above 1 amu. In general, quadrupole mass spectrometers have a difficult time providing reliable and accurate data at low masses (i.e. at or below 4 amu). Two different factors affect low mass readings: The first is known as the "zero blast" problem, where zero blast signals correspond to a mass independent signal that floods and overwhelms the detector at low masses, while the RF/DC fields are too low to stop all ions from reaching the detector. The extent of the zero blast problem depends on the physical dimensions of the filter, the frequency of the RF, and the energy of the ions that traverse the length of the quadrupole filter. Very few QMS systems are capable of displaying atomic hydrogen signals at 1 amu, and in some QMS systems can even affect the detection limits for helium leak detection at 4 amu. Second, all quadrupole mass spectrometers overestimate the concentration of low mass ions when operated in constant absolute resolution mode. It is not unusual for a standard QMS to provide hydrogen partial pressure values that obviously exceed even the total pressure values reported by hydrogen-calibrated total pressure gauges located on the same chamber. The ITMS system mass ejection system is not impacted by zero blast issues and the ratiometric operation ensures that the low masses are accurately represented down to 1amu as shown in Figure 5 where there is very good definition of monatomic Hydrogen to He at 4 amu.

Besides spectral resolution, another important factor which affects the quality of the spectral output of a mass spectrometer is proper calibration of the mass axis scale. In a QMS system, calibration of the mass axis requires carefully adjusting the mass axis scale of the instrument

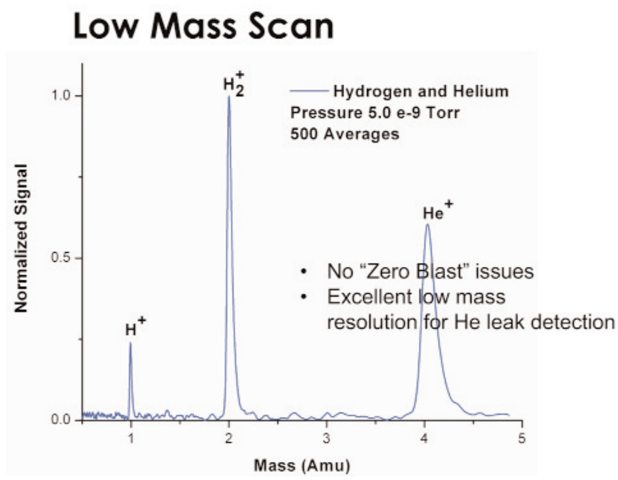


Figure 5: Low Mass Scan

using two independent gas standards of known molecular weight, i.e. two-point calibration. In general, a low mass (i.e. <10 amu) and a high mass (i.e. >80% of the mass range) standard must be simultaneously available to properly calibrate the mass axis. Most two-point calibration procedures are slow, complicated, and do not allow dynamic correction of the mass axis calibration during operation. For an ITMS system, the mass-specific oscillation frequency is directly dependent upon the physical dimensions of the Ion Trap and the Amplitude of the trapping potential. Therefore, once the extraction conditions for a single m/z are known, then all other m/z can be calibrated to the single gas. This allows for a rapid and easy single point calibration based upon gauge manufacturing dimensional control or through a single gas calibration. For example, detecting a water peak (18 amu) in the ITMS device allows for full calibration of the entire 1-300 amu range. This a key ease-of-use benefit for newly manufactured and field supported equipment.

The low power RF drive and electrostatic operating power requirements of the ITMS transducer allows it to be operated at the end of a cable or integrated into a modular form (integrated electronics and sensor). Most QMS instruments require a close physical and electrical coupling of the high power RF drive electronics with the quadrupole transducer and are available only in the modular form. For the ITMS device, a cable can be used to connect to the drive electronics. Combining the ability for remote cable operation, the small size of the ITMS device and the ability for a smaller electronics packaging, an ITMS system provides additional flexibility for installation on a crowded vacuum tool.

Characteristics of the Ion Trap

Table 1: Comparison of ITMS & Quadrupole MS

Feature	Ion Trap MS	Quadrupole MS
Mass Range (amu, low mass range devices)	300*	300
Minimum Detectable Partial Pressure (Torr)	10^{-12}	10^{-13}
Spectral Resolution ($M/\bullet M_{50\%}$)	100 to 300	100 to 300
Scan Speed (1-100 amu scan range)	<0.1sec	1-2sec
Maximum Operating Pressure (Torr)	10^{-5} to 10^{-4}	10^{-5} to 10^{-4}
Surface Area (1-300 amu capable)	Smaller	Larger
Low Mass Range Limit (zero blast)	No	Yes
Calibration	Single Point/Self	Multipoint
Remote Mounting (via cable)	Yes	No

* 1 to 135 amu when used with the Series 830 VQM Controller;
1 to 300 amu when used with the Series 850 VQM Controller

Table 1 compares the low mass range systems based upon ITMS transducers and QMS transducers. The Mass Range for both technologies is shown as up to 300 amu to represent the low-mass type range of interest, although both technologies are capable of higher mass range transducers. The Minimum Detectable Partial Pressure is shown as 10^{-12} Torr for the ITMS device and 10^{-13} Torr for the QMS device; however, stringent UHV surface preparation and memory effects must be considered at these partial pressure detection levels. The Spectral Resolution typical values are shown for these types of devices and are adequate for the 1-300 amu application where these devices are used. The Scan Speed for the ITMS is much faster than the QMS, where the speeds of the ITMS device can be considered for closed-loop control and transient event detection applications. The Maximum Operating Pressure shows equal performance that is limited by the mean-free path within the sensors; however, smaller quadrupole transducers can go into the 10^{-3} to 10^{-2} Torr range at the expense of higher cost, poor resolution, and limited dynamic range. Surface Area is listed as a smaller/larger comparison, where the ITMS device has a smaller surface area due to its smaller size and simplicity of construction, and is an important consideration when minimizing surface area exposed to vacuum. Low Mass Range Limit is shown because of the known zero blast issue with QMS devices that is not present in ITMS devices, and should be considered if the user's application requires accurate measurement at or below 4 amu. Calibration shows another fundamental difference between the QMS and ITMS designs, where the single-gas calibration of the ITMS device is much simpler than the multi-gas calibration of the QMS. Remote Monitoring references the ability to remotely mount the ITMS sensor from the drive electronics which can be of benefit for crowded vacuum systems where there is insufficient room to accommodate both the Quadrupole sensor and drive electronics into a single available space.

Conclusion

QMS systems were the workhorses of the low mass range mass spectrometry industry, especially for residual gas analysis, leak detection and contamination monitoring. Granville-Phillips has developed an Ion Trap Mass Spectrometry technology that will out perform the QMS in the majority of these applications. In addition to performance advantages, the ITMS system is easier to use and maintain. The combination of the better performance and ease-of-use will allow ITMS systems to replace QMS as the industry workhorse.

BROOKS AUTOMATION

Brooks Automation, Inc. / Granville-Phillips Product Center
6450 Dry Creek Pkwy • Longmont, Colorado 80503-9501 USA
Telephone: +1-303-652-4400 • Toll free in USA +1-800-776-6543 • Fax: +1-303-652-2844
email: VQM@brooks.com Visit us online at: www.brooks.com