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Comparison of Ion Trap Mass Spectrometer and Quadrupole Mass Spectrometer

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This paper on the Granville-Phillips Vacuum Quality Measurement (VQM™) system was presented at the 2009 Society of Vacuum Coaters TechCon as an emerging technology.

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This paper was published in the 2009 SVC TechCon Proceedings and is made available with permission of the SVC.



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ABSTRACT

The use of Electrostatic Ion Trap technology for low-mass range mass spectrometry applications is new and overlaps with the common Quadrupole-based mass spectrometer. An overview of the fundamental principles, key specifications and performance differences of the Electrostatic Ion Trap and Quadrupole mass spectrometer technologies will be compared and contrasted.

INTRODUCTION

Mass spectrometry (MS) is an analytical technique widely used to (1) determine the molecular mass of individual and/or unknown compounds, (2) analyze the chemical composition of complex gas samples, (3) perform structural analysis of individual or unknown chemicals, (4) verify the identity and purity of known substances and (5) provide data on isotopic analysis.

Mass spectrometry is widely recognized as a very powerful and valuable gas analysis technology with applications in both research and industrial fields. It is well understood by both process engineers and research scientists that knowing the chemical composition of a vacuum environment is generally more powerful than simply tracking the total pressure of the vacuum chamber. Monitoring and controlling the partial pressures of the gas components in a vacuum process or experiment has generally led to dramatic yield and productivity improvements throughout the vacuum coating industry.

Mass spectrometers of small size and limited mass range, often called residual gas analyzers (RGA) or partial pressure transducers, have been used routinely for over three decades to monitor vacuum-based processes and to provide real-time gas composition analysis. Most commercially available RGAs are relatively small and rugged mass spectrometers, specifically designed for process control and contamination monitoring in the semiconductor and vacuum coating industries. RGAs are commonly used to monitor the quality of the vacuum and detect minute traces of impurities in low-pressure gas environments. These impurities can be measured down to UHV levels, with ppm detection limits in the absence of background interferences. RGAs are also used as sensitive in-situ helium leak detectors providing the ability to perform dynamic leak checks. In recent years, RGAs have also found an increasing

number of applications in new areas including surface science, catalysis, environmental monitoring, homeland security and direct real-time analysis (i.e. replacing gas chromatography) for the chemical, oil, food and packaging industries.

The MS principle of operation consists of ionizing chemical compounds followed by separation, detection and measurement of the resulting charged molecules and fragments based on their individual mass-to-charge ratios (m/z). In a typical MS procedure, a gaseous sample is loaded onto the MS instrument, and its compounds are ionized by different methods, resulting in the formation of charged particles (i.e. ions). The resulting ions are separated based on their individual m/z values and directed towards a detector which measures the abundances of each ion present in the gas mixture. The MS technique is capable of providing both quantitative and qualitative partial pressure information.

Mass spectrometers are differentiated based on the ionization methodology used to generate charged particles and the analysis technique used to separate the ions based on their individual m/z values. At their most basic level, mass analyzers can be differentiated based on whether trapping or storage of ions is required to enable mass separation and analysis. Non-trapping mass spectrometers do not trap or store ions, and ion densities do not accumulate or build up inside the device prior to mass separation and analysis. Common examples include quadrupole mass filter and magnetic sector mass spectrometers in which a high power dynamic electric field or a strong magnetic field sector, respectively, are used to selectively stabilize the trajectories of ion beams of a single m/z value. Trapping spectrometers can be subdivided into two subcategories: Electrodynamic traps such as for example the quadrupole ion traps (QIT) of Paul's design, and electrostatic ion traps (ESIT) such as the electrostatic confinement traps more recently developed. Magnetic sector mass spectrometry has been standard in most commercially available leak detectors and used to be the technology of choice (along with competing time-of-flight systems) before quadrupoles became the reigning standard. QITs are standard tools in many analytical chemistry laboratories but have found limited application in vacuum process applications due to their narrow pressure dynamic range. Until very recently, purely electrostatic ion traps were physically too large and difficult to operate, not suitable for residual gas analysis and incompat-

ible with process monitoring/control applications. However, a novel Electrostatic Ion Trap technology concept presently under development at the Granville-Phillips® Product Center of Brooks Automation, Inc. provides a promising new way to perform real time partial pressure gas analysis with high sensitivity, unlimited mass range, ultrafast scan rates from a very small sensor package, i.e. not any larger than a standard total pressure ionization gauge.

QUADRUPOLE MASS SPECTROMETERS

Most commercially available RGAs rely on electron impact ionization (EII) for ion formation very similar to what is found in hot cathode ionization gauges. A large majority (i.e. >95%) of RGAs also rely on quadrupole mass filters to separate the resulting ions based on their m/z values. The quadrupole mass filter consists of four parallel metal rods with each opposing rod pair connected together electrically and a combination of radio-frequency (RF) and direct (DC) voltage applied between one pair of rods, and the other. Ions travel down the quadrupole, in between the rods, and only ions of a certain m/z will reach the detector for a given RF/DC ratio (i.e. other ions have unstable trajectories and will be lost to the walls through collisions). This allows filtering of an ion with particular m/z (single ion monitoring), or scanning a range of m/z -values by continuously varying the voltages (mass spectrum generation).

Key specifications for mass spectrometers include: (1) mass range, (2) minimum detectable partial pressure limit, (3) spectral resolution, (4) scan speed and (5) maximum operating pressure. The mass range (i.e. highest detectable m/z value) of a typical commercially available RGA, based on quadrupole mass analysis, is <300 atomic mass units (amu) and is generally limited by the maximum amplitude of RF that can be safely delivered from a reasonably sized electronics package. The maximum pressure of operation is typically less than 10^{-4} Torr and limited by the requirement to keep the size of the sensor less than the mean free path of the gas molecules in the vacuum system. Scan times usually exceed 1.5 s for a full 1-100 amu scan range and are limited by the response time of resonant RF power sources. Minimum detectable partial pressures are between 10^{-9} and 10^{-13} Torr, generally limited by the performance specifications of typical electrometers and dependent on whether an electron multiplier is available as an option. Nominal mass resolution specs (i.e. indicating the widths of the individual peaks in the mass spectrum) are typically $\Delta M_{50\%} < 1$ amu (i.e. peak width at 50% peak height) over the entire mass range of the device and limited by the frequency of the RF and the physical dimensions of the quadrupole.

Most RGA systems pack some alternative means of collecting coarse total pressure readings and/or provide auxiliary analog or digital input ports to collect total pressure readings from auxiliary gauges mounted on additional ports of the vacuum

system. Some commercial offerings also provide analog and digital I/O ports to allow closed loop process control based on partial pressure readings as well as stand-alone software packages to collect and display mass spectrometry data.

Due to the large RF power requirement of quadrupole mass analyzers (i.e., typically $10 V_{pp}$ of RF amplitude per amu is required), most quadrupole rod assemblies are powered by carefully tuned resonant RF circuits which require direct physical connection between the vacuum sensor head and the electronics. This requirement can be a problem when bakeout or physical constraints require separating the sensor from the electronics during operation.

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 quadrupole mass spectrometer, calibration of the mass axis requires carefully adjusting the mass axis scale of the instrument using two 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) 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.

Most commercially available RGAs 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. In first place all quadrupole mass filters are susceptible to the “zero blast” problem. The zero blast signal corresponds to a mass independent signal that floods and overwhelms the detector at low masses and 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 RGAs are capable of displaying atomic hydrogen signals at 1 amu, and in some cases, the zero blast can even affect the detection limits for helium leak detection at 4 amu. In addition all quadrupole mass spectrometers overestimate the concentration of low mass ions when operated in constant absolute resolution mode. It is not unusual for standard RGAs 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.

Unlike ion traps, where ions are accumulated and stored, the ion signals collected by a quadrupole are strictly proportional to the partial pressures of the individual gases in the chamber. A typical RGA will have a sensitivity of 10^{-4} A/Torr, providing a detection limit of 10^{-10} Torr for an electrometer with

a typical 10 fA noise floor. Ion traps accumulate ions and generally show higher sensitivities at UHV levels without requiring high end electrometers.

A NOVEL ION TRAP MASS SPECTROMETER

Electrostatic Ion Trap technology is being used in mass spectrometers [1] today. The relatively recent Orbitrap mass spectrometer, recognized for its high-mass range and high-resolution, is now offered by major equipment suppliers. The Orbitrap was developed by A. Makarov (US Patent 6,872,938) in 1999 as an improvement to the Kingdon Trap (1923) and is a viable replacement for Fourier transform ion cyclotron resonance MS systems. The trap has simple and small construction of two outer electrodes and an inner electrode. In an Orbitrap the ions are injected tangentially into the electric field between the outer and inner electrodes and are trapped by their electrostatic attraction to the inner electrode that is balanced by centrifugal forces pushing the ions away from the inner electrode. The frequency of oscillation is inversely proportional to the m/z . The ion's rotation is electrically detected and converted to mass specific information (mass detection). Orbitrap Mass Spectrometers have a high mass accuracy of 1-2 ppm, high resolving power and a high dynamic range. The UHV operation of the Orbitrap reduces its flexibility as a general purpose mass spectrometer instrument that must natively operate from UHV to HV.

Electrostatic ion confinement traps in which the ions oscillate in a reflective linear motion between two opposite electrostatic mirrors are also presently available. The ions are injected through a stack of electrodes, which are used as

electrostatic mirrors. The stability criterion of such a trap is similar to the one existing for photons trapped in an optical resonator. A harmonic potential trapping well is required to ensure ion energy independent oscillations along the axis of the cylindrical trap with oscillation periods strictly related to $m/z^{1/2}$ and independent of amplitude. These traps are generally large (tens of centimeters), require very careful and accurate mechanical design to assure harmonicity of the potential and operate only at UHV levels (i.e. to avoid losses of ions to collisions with residual gas). Mass analysis in these traps has been performed through (1) use of remote, inductive pickup and sensing electronics and fast Fourier transform (FFT) spectral de-convolution [2] or (2) sudden ion extraction by rapid switching on/off of the high voltage trapping potentials [3]. In the second detection scheme, all the ions escape as the gate is open and the m/z values are detected through a simple time-of-flight analysis.

A novel and recent practical Electrostatic Ion Trap technology that is appropriate for low-mass range general purpose use is the anharmonic resonant electrostatic trap mass spectrometer (ARTMS) shown in the SIMION® simulation of Figure 1. The ARTMS is a simple electrostatic mirror structure of cylindrical symmetry with a center plate (i.e. central lens) biased at a negative 1000 V (-1000 V, nominal) located between two opposite grounded cup structures (i.e. electrostatic mirrors) biased at zero volts (0V, nominal). The biasing structure creates an electrostatic field as shown by the electrostatic equipotential lines. The center plate has an aperture (dimension "A") that focuses the path of the ions within the trap. The horizontal path of the ions is shown, where the amplitude of oscillation is less than the length "L/2". The relationship between

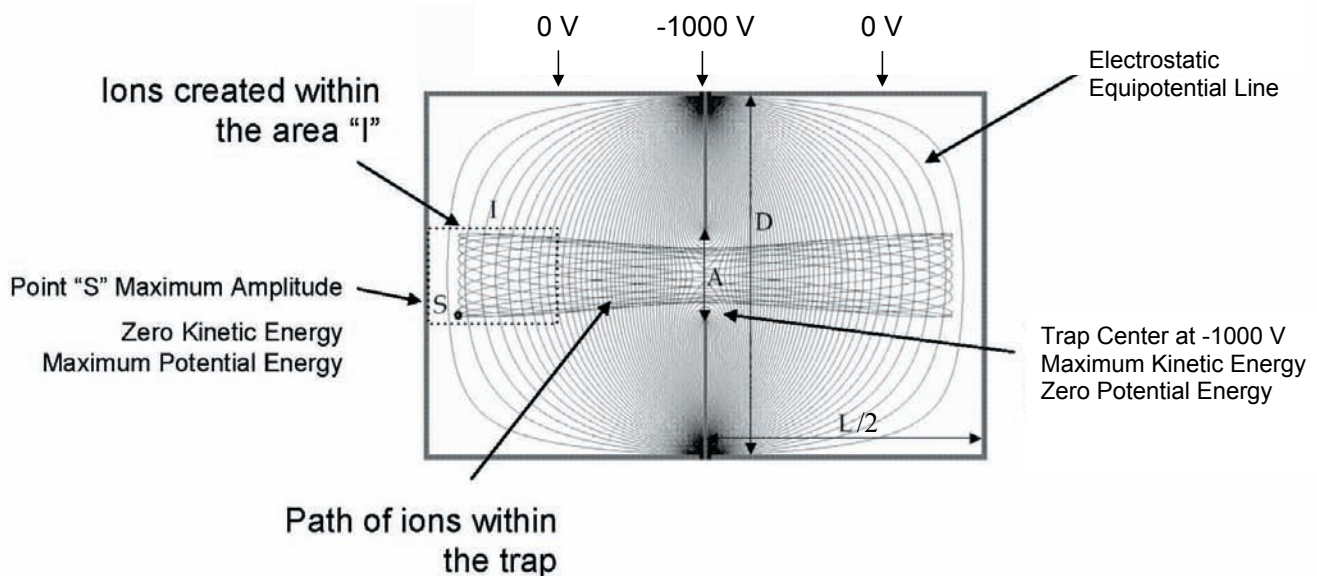


Figure 1: SIMION simulation of the Anharmonic Resonant Electrostatic Trap Mass Spectrometer (ARTMS).

the length “L” and the diameter “D” of the trap determines the amount of total charge that can be stored within the trap and the stability of ion trajectories due to the shaping of the equipotential lines. Not shown in the diagram is the inlet (i.e. an aperture on the left side of the figure) and the outlet (i.e. an aperture on the right side of the figure).

The ions oscillate horizontally along the axis of the cylindrical trap at a resonant frequency that is inversely proportional to the square root of their m/z [4]. 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 “S”, 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 , have approximately the same PE at point “S”. 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 has been developed to selectively increase the energy, and therefore the amplitude, of the ions until their amplitude exceeds length $L/2$ and the ions are ejected from the trap and detected.

CHARACTERISTICS OF THE ANHARMONIC RESONANT ION TRAP

The nature of the ARTMS device is to rapidly fill with ions from a sample of gas to be analyzed, with each gas component oscillating at its own resonant frequency. The energy requirement to selectively eject a sequence of m/z ions is very small and can be done using low power electronic signals. This allows for the rapid scanning of the complete 300 amu range within 200 ms and 100 amu range in less than 70 ms. This scan rate is much faster than the typical 1-2 s 100 amu scan speed associated with typical quadrupole mass spectrometers.

This speed advantage can be used in two ways: (1) as an ultra-fast measurement instrument in closed-loop control system, and (2) for additional measurement averaging to improve signal-to-noise ratio for trace level contamination control. In Figure 2 we compare a 1-100 amu scan rate (speed) of a fast quadrupole to the ARTMS. The top scans show how much information you get from a 70 ms single scan, where the fast quadrupole has a small sliver of information while the ARTMS has performed the full 1-100 amu scan with good detection limits while still exceeding the response times of most mass-flow control devices. The bottom scan runs the quadrupole at full speed, 1.5 s for a 1-100 amu scan, while the ARTMS has averaged approximately $qty=20$ 1-100 amu 70 ms scans. The Quadrupole single scan shows good performance; however, there is more noise than the comparable ARTMS device, and the ARTMS detected trace levels of water and

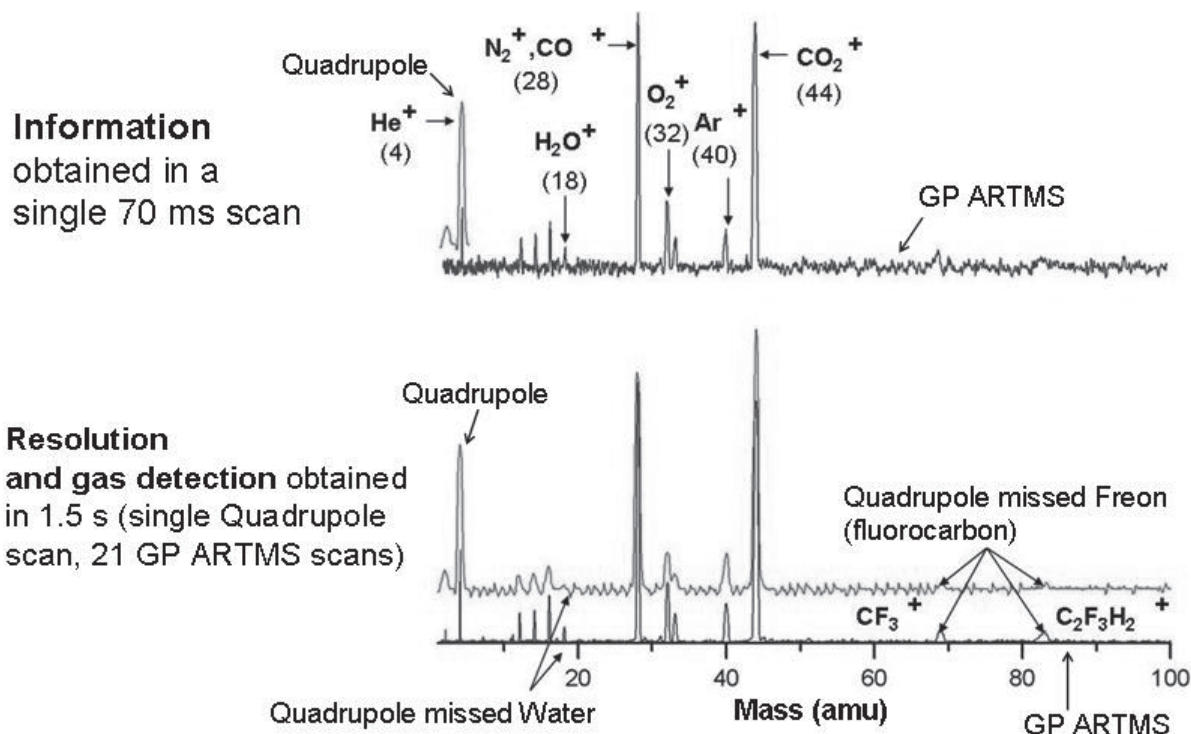


Figure 2: Scan Rate (Speed) Comparison of Quadrupole MS and ARTMS.

Freon that were missed by the Quadrupole. Figure 3 shows an ARTMS 5 ms single scan (not averaged) for detecting an air leak, where the scan range was limited from 15 amu to 40 amu. It can also be seen in Figure 3 that trace levels of water were detected in this ultra-fast 5 ms scan. The combination of high sensitivity and high speeds makes the ARTMS device the new standard for fast closed-loop process control based on compositional analysis.

Electrostatic repulsion between ions in the oscillating beam leads to space charge limitations which ultimately fixes the density of charge that can be stored in the ARTMS device, and is related to the length (L) and diameter (D) – a larger trap can store more ions and a smaller trap can store fewer ions. This property is largely pressure independent and the amount of charge stored within the trap is relatively constant over its usable range, and therefore the performance of the trap is more consistent over its usable range. Consequently the speed and sensitivity advantage of the ARTMS relative to a quadrupole MS increases with decreasing pressure, making the new trap technology ideal for ultra high vacuum (UHV) applications. The Granville-Phillips 1-300 amu ARTMS

device (Electron Source, Ion Trap and Detector) is about the same size as our standard total pressure ionization gauge (4 cm in diameter x 13 cm length). The small size of the ARTMS device has less surface area that is exposed to vacuum than most full range quadrupole devices to minimize outgassing and process memory effects.

Another characteristic of the ARTMS 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 ARTMS 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 ARTMS device.

Because the ARTMS stores a fixed amount of charge, the sensor is intrinsically a ratiometric device, where the maximum ion charge is a fixed 100% and the gas component partial pressures represent a portion of the 100%. In many applica-

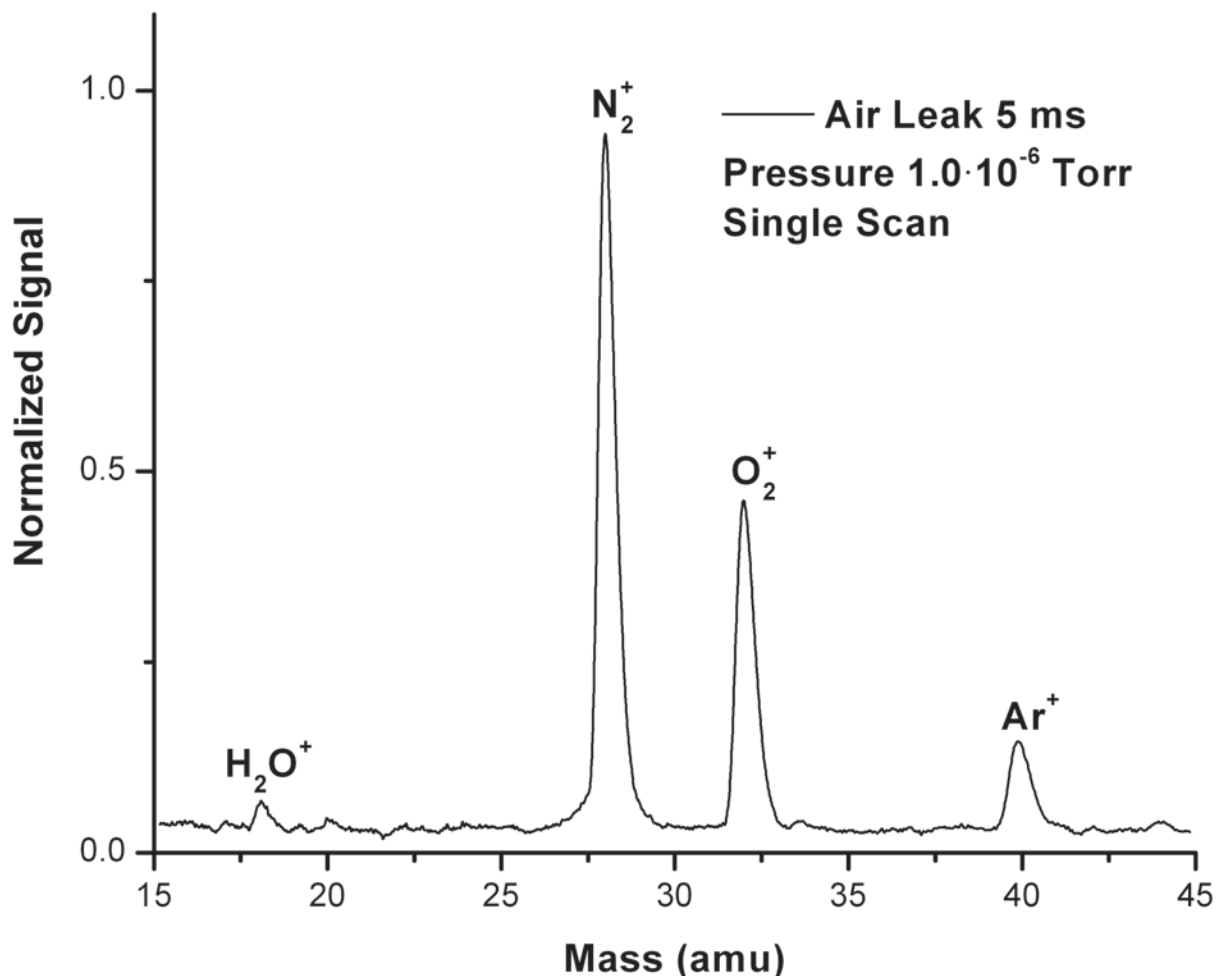


Figure 3: Fast scan for air leak in 5 ms single scan.

tions where concentrations need to be tracked and reported, ratiometric information is preferred over absolute partial pressure information and is a native output of the ARTMS device. Where absolute partial pressure information is needed, the output of the ARTMS can be easily scaled using total pressure information to provide partial pressure outputs.

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

The mass-specific oscillation frequency of the ARTMS device is largely dependent upon the physical dimensions of the Ion Trap and the amplitude of the trapping potential, and is

not dependent on the drive electronics. 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 ARTMS device allows for full calibration of the entire 1-300 amu range. This is an important ease-of-use benefit for both newly manufactured and field supported equipment.

Many Quadrupole MS devices cannot accurately measure below 2-to-4 amu due to zero blast limitations; therefore the Quadrupoles' 1-300 amu range is more accurately a 2-300 amu or 4-300 amu range. The ARTMS by design does not have the zero blast effects and can fully resolve all the lower amu peaks at full sensor resolution and is shown in Figure 4. Therefore, a permanently installed ARTMS device could easily be used as an in-situ helium leak detector, in portable leak detector applications and as an efficient isotopic ratio mass spectrometer.

RGAs based on quadrupole mass analyzers usually operate in constant mass resolution mode. As a result, the throughput

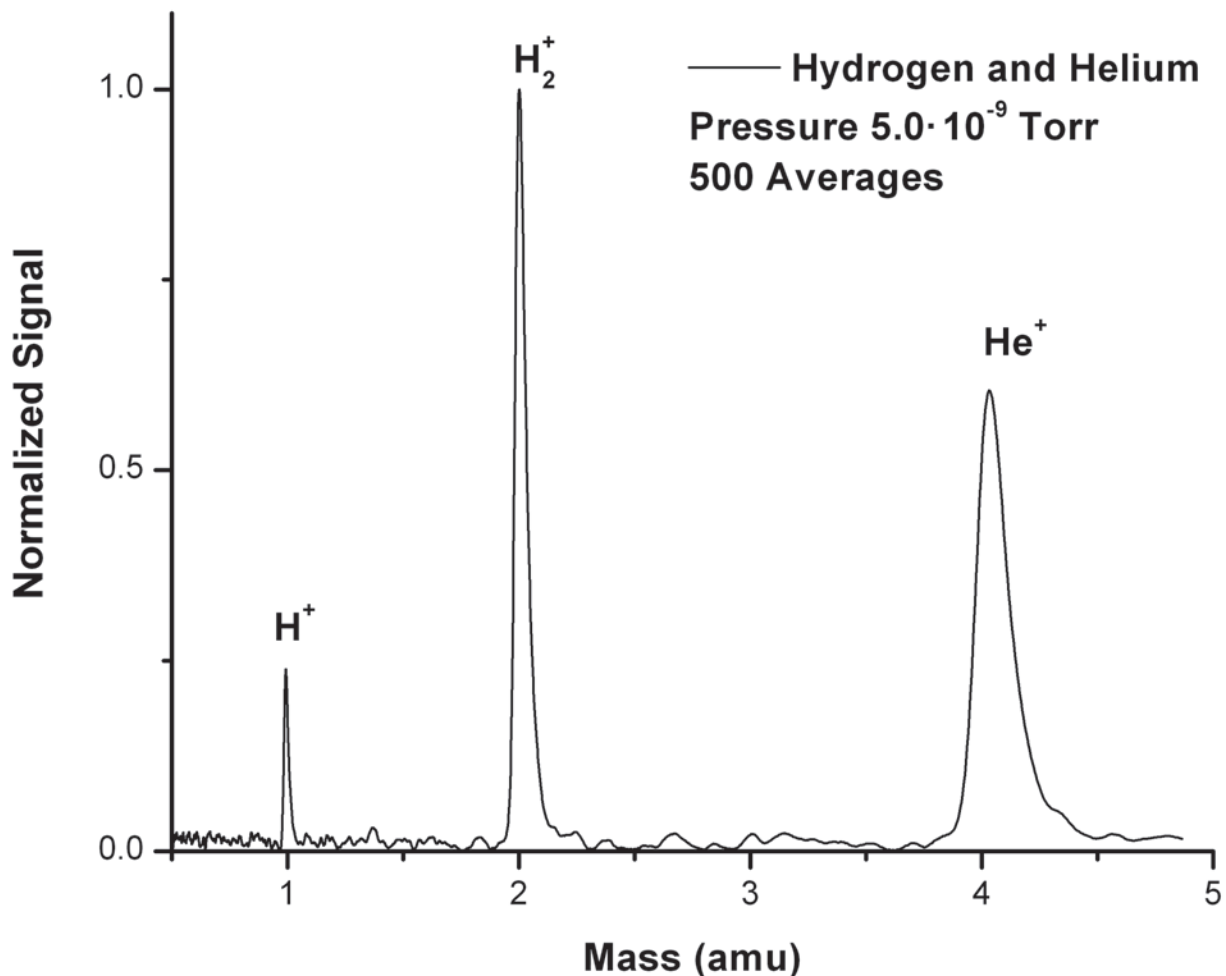


Figure 4: Low mass scan capabilities of the ARTMS sensor.

of quadrupole mass filters is mass dependent. As the mass of the ions increases, their radial oscillation amplitudes increase and more ions are lost to collisions with the rods. As a result, quadrupole mass spectrometers lose sensitivity as the mass of the ions increases. ARTMS stores all ions inside the trap and preserves the relative concentrations of the ions during ejection, providing a more accurate representation of gas concentrations for the sample gas.

ARTMS sensors do not technically have an upper mass limit, or mass range. In fact, ARTMS traps have been shown to provide mass information well above the 600 amu range. However, most volatile chemical substances have a molecular weight below 300 amu, and the electronics and data acquisition software is typically limited to a mass range of 300 amu to support these applications.

Table 1 compares the ARTMS to the Quadrupole MS. 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 ranges. The Minimum Detectable Partial Pressure is shown as 10^{-11} Torr for the ARTMS device and 10^{-13} Torr for the quadrupole MS; 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 ARTMS is much faster than the Quadrupole MS, where the ARTMS device can be considered for closed-loop control and transient event detection. The Maximum Operating Pressure shows equal performance that is limited by the mean-free path within the sensors; however, smaller quadrupoles can go into the 10^{-3} to 10^{-2} Torr range at the expense of higher cost, resolution and dynamic range. Surface Area is listed as a smaller/larger comparison, where the ARTMS 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 Quadrupole MS devices that is not present in ARTMS device, and should be considered if the users' application requires measurement below 4 amu. Calibration shows another fundamental difference between the Quadrupole and ARTMS designs, where the single-gas calibration of the ARTMS device is much simpler than the multi-gas calibration of the Quadrupole MS, and where ARTMS self-calibration methods can be considered. Remote Monitoring references the ability to remotely mount the ARTMS sensor from the drive electronics that 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.

Table 1: Comparison of ARTMS & Quadrupole MS.

Feature	ART MS	Quadrupole MS
Mass Range (amu, low mass range devices)	300	300
Minimum Detectable Partial Pressure (Torr)	10^{-11} to 10^{-9}	10^{-13} to 10^{-9}
Spectral Resolution ($M/\Delta M_{50\%}$)	100 to 300	100 to 300
Scan Speed (s, 1-100 amu scan range)	<0.1	1-2
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

CONCLUSION

Today low mass range quadrupole mass spectrometers are the workhorses of the industry, especially for residual gas analysis, leak detection and contamination monitoring. A novel Electrostatic Ion Trap technology can now be applied to these same applications and provides similar performance in terms of mass range, pressure range, sensitivity and mass resolution. The Anharmonic Resonant Trap technology has demonstrated advantages in terms of ease-of-use, point-sample capabilities and transient detection, performance stability over the UHV to HV pressure range, simplicity in calibration and ultra-fast scan speed. Finally, the fundamental nature of the Electrostatic Ion Trap's ratiometric measurement offers capabilities for the point sampling of the gas to be measured and the ability to provide native ratiometric information or easily scaled partial pressure information.

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