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Autoresonant Trap Mass Spectrometry (ART MS) for remote sensing applications

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ABSTRACT

A novel mass spectrometer is described that uses purely electrostatic fields to store ionized gases within a cylindrical ion trap. Ions are generated directly inside the trap by electron ionization of gas molecules. An anharmonic trapping potential well confines the ion trajectories of all ion masses, and of a wide range of initial energies, to stable oscillatory motions along the axis of the trap. Mass selective ejection is achieved through a novel autoresonant energy pumping process. The new mass spectrometer has unlimited mass range, good sensitivity at high and ultrahigh vacuum levels, very fast scan rates, compact construction, and extremely low power requirements as it uses only static bias potentials and very small RF signal levels (in the 100 mV range). Small size, low power consumption, rugged construction and reliable operation make ART MS technology an ideal candidate for in situ mass spectrometry in a wide variety of remote sampling applications including harsh sampling environments. Fast mass spectra acquisition rates particularly attractive for sampling applications from fast moving platforms such as airplanes, rockets and boats.

1. Introduction

The deployment of mass spectrometry instrumentation for in situ chemical analysis in a wide variety of harsh environments, imposes very strict requirements on the reliability, ruggedness, size, speed and power consumption of compatible mass spectrometer sensors. Mass spectrometers of small size and limited mass range are often called residual gas analyzers (RGA), partial pressure analyzers or partial pressure transducers, and are generally based upon quadrupole mass filter (QMS) designs. These measurement instruments have been used for over three decades for contamination monitoring, chemical analysis and as vacuum diagnostic tools. QMS partial pressure transducers are generally too large for field deployments, require high power (i.e., 20–30 W) to operate and are slow (i.e., 1–2 s measurement times for range of gases of interest). Several alternative sensing technologies based on quadrupole ion traps, miniaturized quadrupole filters, rotating field and magnetic sector mass spectrometers have been tested and used in connection to field deployments, but the search continues for the “ideal” sensor for harsh environment applications [1].

An Ion Trap Mass Spectrometer (ITMS) based on purely electrostatic ion storage in an anharmonic potential was recently disclosed by Ermakov and Hinch [2]. The new trapping technology allows to mass selectively eject and detect ions formed by electron ionization directly inside a cylindrical trap based on a novel energy pumping phenomenon called autoresonance [3]. A commercial version of an Autoresonant Trap Mass Spectrometer (ART MS) is under development at Granville-Phillips Instruments, Brooks Automation, Inc. that offers the small size, low power, fast response times and rugged design demanded by a wide variety of in situ sampling applications, including harsh environment conditions. The present ART MS sensor provides 1–300 amu scan range, resolutions exceeding 250×, includes a field replaceable hot-filament ionization assembly, ultrahigh vacuum compatible construction, an electron multiplier detector and a small controller based on a single 3 in. × 6 in. electronics board. The entire sensor is approximately 15 cm in length, with a 2.5 cm ion trap component. The improved ART MS detector provides fast sampling speeds of approximately 70 ms for 1–100 amu scans. Total power consumption is less than 7.5 W during operation. Remote gauge cable connection to the controller electronics makes it possible to embed the sensor and electronics into compact sampling system setups and a very simple user interface, including a command interface based on the Standard Commands for Programmable Instruments (SCPI) communication protocol, allows easy integration into any pre-existing data acquisition system [4].

2. The Ion Trap Mass Spectrometer (ITMS)

The ITMS is a practical low-mass range electrostatic ion trap design that uses an anharmonic resonant electrostatic trapping potentials as shown in the SIMION® simulation [5] of Fig. 1. ITMS

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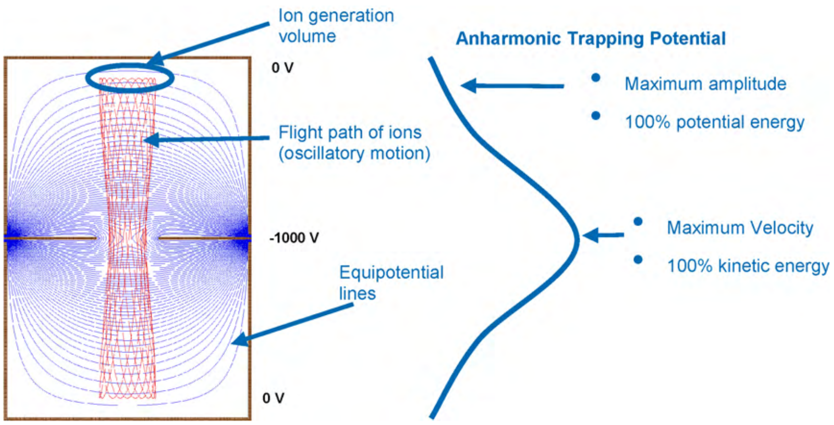

Fig. 1. Electrostatic ion trap.

design is a simple electrostatic mirror structure of cylindrical symmetry with a center plate biased at a negative 1000 V dc 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 path of the ions within the trap is shown in Fig. 1, where the amplitude of oscillation is less than the length of the trap. For clarity we do not show inlet and the outlet structures of the ITMS.

The ions oscillate back-and-forth within trap 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 the kinetic energies during an oscillatory 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, have approximately the same initial PE. 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 $(1/2)mv^2$. 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 based on autoresonant excitation has been developed to mass selectively increase the ion energy using low power RF signals until their amplitude exceeds the length of the trap where the ions can be detected. The details of the autoresonant energy pumping process and ion ejection and detection mechanisms have already been described by Ermakov and Hinch [2] and will not be repeated here.

The benefits of the ART MS design are first, fast spectral scans, i.e., 20× (or more) faster than a typical QMS. Second, low power consumption due to purely electrostatic ion storage and small RF signal drive. Third, ultrahigh vacuum (UHV) compatibility due to small size and reduced surface areas (i.e., minimized outgassing and sample memory). Fourth, excellent low-mass performance, with no Zero Blast issues [6]. Finally, point sample of the gases since the ionization occurs directly inside the mass separator.

Fig. 2 shows the comparison between the Ion Trap (ITMS) and the QMS performance. Two sets of device scans are shown. QMS data was collected with a Stanford Research Systems, SRS RGA200 operated in Faraday Cup mode and running at the fastest possible scan rate (i.e., roughly 1.56 s for a 100 amu range scan). Both top and bottom scan sets are over the same 1–100 amu mass (m/z) scan range and all measurements were performed at a constant 1×10^{-7} Torr. The top scan set (scans A and B) was run at 70 ms, the time for the ITMS to complete a 1–100 amu scan. The bottom scan set (scans C and D) was run at 1500 ms, the time for the QMS to complete a 1–100 amu scan.

The ITMS scan (A) in the top scan set shows low noise and good single-shot resolution. The range of commonly used gas 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 (B) shows how much information you get from the QMS transducer in the same 70 ms period, where only helium was detected and over represented (too large a peak) due to QMS zero blast [6] issue.

Fig. 2 bottom scan set shows the 1500 ms duration single-shot QMS scan (C) with the measurement of the major helium, nitrogen, oxygen, argon and carbon dioxide peaks. Like in the top QMS scan (B), the helium peak is overrepresented due to zero blast. The ITMS scan (D) shows a noise reduced and highly defined measurement through the averaging of 21 scans during the same measurement period. The ITMS measurement also clearly shows water and freon peaks that were missed by the QMS.

Fig. 3 shows an ITMS 5 ms single scan (not averaged) for detecting an air leak, where the scan range was limited from 15 to 45 amu. Clearly, ART MS technology has the capability to deliver

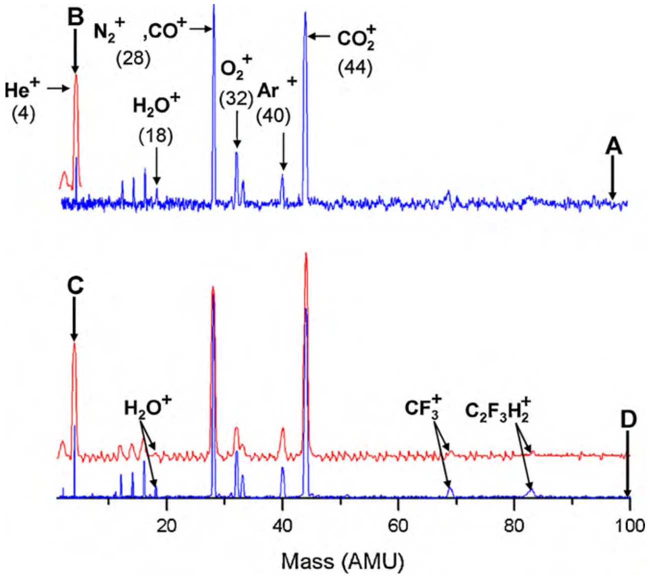

Fig. 2. Comparison of mass spectra obtained with QMS vs. ART MS technology.

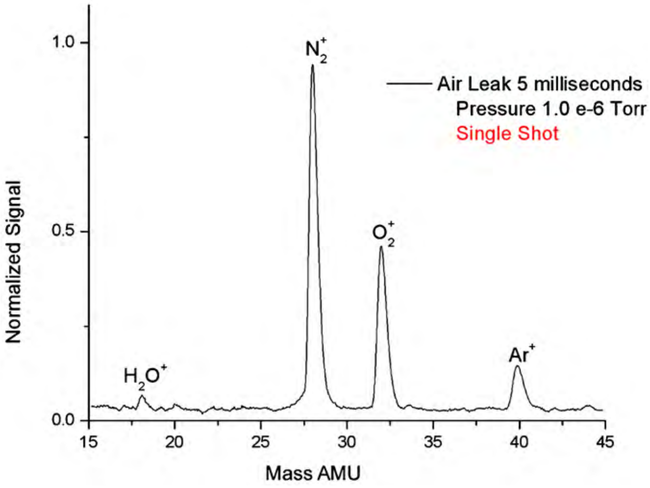

Fig. 3. Fast scan of air.

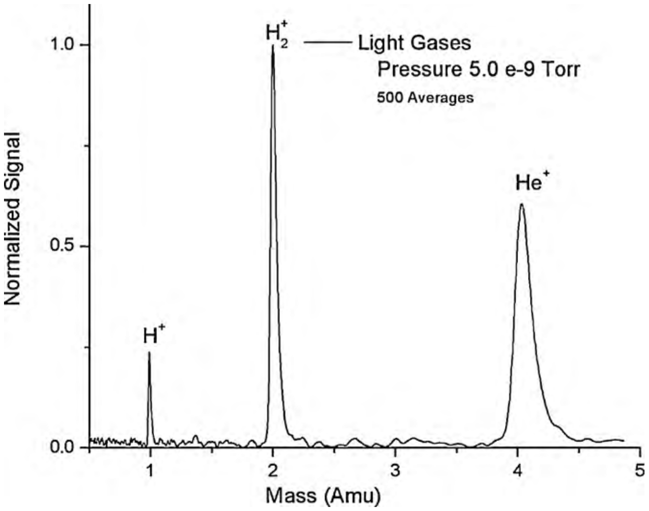

Fig. 4. Low-mass range scan.

very fast mass spectrometry scans, and is also capable of scanning over user-selectable mass ranges.

The ITMS is an electrostatic device, in which electrostatic repulsion between ions in the oscillating beam leads to space charge saturation which ultimately limits 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, and 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 small size of the ITMS 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 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 two examples of the large range of 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 total pressure information to provide absolute 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 factor is known as the “zero blast” problem [5], where 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 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. 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 QMS to provide hydrogen partial pressure values that obviously exceed even the total pressure values reported by hydrogen-calibrated total pressure gauges located in the same gas chamber. The ITMS mass ejection system is not impacted by zero blast issues and the ratiometric operation ensures that the low masses are accurately represented down to 1 amu as shown in Fig. 4 where there is very good definition of monatomic Hydrogen to He at 4 amu. The high resolution of ART MS sensors at low masses makes them potential candidates for isotopic ratio mass spectrometry measurements.

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 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) must be simultaneously introduced into the gas environment to properly calibrate the mass axis. Most two-point calibration procedures are slow, complicated, operator driven 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 (i.e., ejection frequency) for a single m/z are known, then all other m/z can be calibrated to the single gas using a very simple calibration algorithm. 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 is a key ease-of-use benefit for newly manufactured and field supported equipment. Fig. 5 shows an example of a mass spectrum collected with an ART MS trap with the x-axis representing the ejection frequencies for the different mass speaks corresponding to common residual gases. The measured frequencies are in close agreement with the ejection frequencies calculated from SIMION ion trap models demonstrating

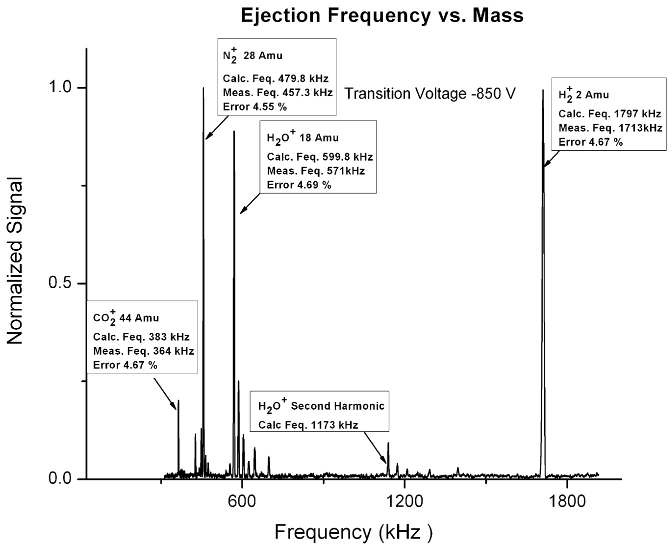

Fig. 5. Ejection frequency vs. mass.

Table 1
Comparison of ART MS and quadrupole MS.

Feature	ART MS	Quadrupole MS
Mass range (amu, low-mass range devices)	300	300
Minimum detectable partial pressure (Torr)	10^{-12}	10^{-13}
Spectral resolution ($M/\Delta M_{50\%}$)	100–300	100–300
Scan speed (1–100 amu scan range)	<0.1 s	1–2 s
Maximum operating pressure (Torr)	10^{-5}–10^{-4}	10^{-5}–10^{-4}
Surface area (1–300 amu capable)	Smaller	Larger
Power (W)	7.5	20–30 (typical)
Zero blast issue	No	Yes
Calibration	Single point/auto	Multipoint/manual
Remote mounting (via cable)	Yes	No
Mechanical requirements (assembly)	Low	High
Contamination buildup rate	Low	High

the ability to calculate accurate ejection frequencies based on geometrical dimensions and bias voltages.

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 very compact gas sampling system.

Another important advantage that separates ART MS technology from quadrupole mass filter and quadrupole ion trap technologies is the fact that contamination buildup does not seem to be an important issue during long periods of operation. All ions generated by electron ionization enter the quadrupole filter or trap, but only one *m*/*z* value exits at a time (i.e., depending on filter RF/DC settings) leaving all other ions behind. The ions that do not exit the quadrupole structure are mostly lost to collisions with internal electrodes and cause the fast accumulation of contaminant buildup. Contamination buildup eventually leads to loss of performance in the quadrupole based mass separator as the operational voltages are affected by dielectric coatings. In an electrostatic ion trap, most ions formed inside the ionization volume find their way out of the trap (i.e., may take a few scans). As a result, ART MS traps seem to be quite impervious to contamination buildup. Our initial observations seem to indicate that ART MS traps should be expected to perform without any performance losses for periods of time exceeding their quadrupole based counterparts.

The fast mass scan speeds delivered by ART MS sensors offer many opportunities previously unavailable in the harsh environment sampling field. Fast scan speeds can be applied to detect brief transients in gas concentrations such as sudden changes in gas emissions from environmental sources. Fast scan speeds can increase the geographical resolution of measurements performed from fast moving platforms such as planes, rockets, balloons, and speed boats. ART MS sensors are fast enough to sample gas peaks eluted from gas chromatography (GC) columns. Modern mass spectrometry sensors interfaced to GC instruments rely mostly on quadrupole ion trap mass spectrometry and double focusing magnetic sector mass spectrometers. Contamination buildup and a lack of scan flexibility are some of the common problems associated with those sensors that will be alleviated by ART MS technology. GC-ART MS sampling systems are expected to deliver small sampling packages with unprecedented low power requirements and long-term stability. We also fully expect ART MS sensors to become interfaced with ion mobility spectrometers in the near future providing new levels of confidence in the sampling and measurement of chemical warfare agents and environmental chemicals.

The rugged design of ART MS traps is expected to contribute to their acceptance in applications involving mechanical vibration and large sudden accelerations, such as rocket launched sampling platforms. The low power requirements of ART MS sampling systems makes them also ideal for sampling platforms such as rovers relying on battery and solar cell power sources.

3. Characteristics of the ion trap

Table 1 compares the low-mass range systems based upon ITMS transducers and QMS transducers [7]. 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 background gas levels 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, transient event detection and sampling from fast moving platforms such as airplanes, speed boats, balloons and submarines. The Maximum Operating Pressure shows equal performance that is limited by the mean-free path within the sensors; however, smaller quadrupoles transducers can go into the 10^{-3}–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. The zero blast issue of QMS devices is not present in ITMS devices, and should be considered if the users' application requires accurate measurement at or below

4 amu. Calibration shows another fundamental difference between the QMS and the 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 that can be of benefit for crowded vacuum systems where there is insufficient room to accommodate both the Quadrupole sensor and the drive electronics into a single available space. Mechanical requirements refers to the fact that no high precision assemblies are required to manufacture an ART MS sensor, resulting in very rugged sensors with very good long-term mechanical stability. Contamination buildup rate refers to the fact that contamination buildup inside ART MS traps has not been an issue in our prototypes operated over periods of time now exceeding two years.

4. Conclusions

We are presently developing an Ion Trap Mass Spectrometry technology that is ideally suited for field studies and harsh environment applications. In addition to performance advantages, the ITMS system is easier to use, maintain and calibrate. We believe that the combination of better performance and ease-of-use will drive ART MS to replace many of the prevalent mass spectrometry technologies presently used in harsh environment gas analysis applications.

ART MS technology is in its infancy. We fully expect significant developments in the fundamental understanding of the core technology, as well as in its range of chemical analysis applications. We predict that the harsh environment gas analysis community of scientists and engineers will be a key driver for all future advances in this novel technology.

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