
Real-Time Quantitative Analysis of H₂, He, O₂, and Ar by Quadrupole Ion Trap Mass Spectrometry

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The use of a quadrupole ion trap mass spectrometer (QITMS) for quantitative analysis of hydrogen and helium as well as of other permanent gases is demonstrated. Like commercial instruments, the customized QITMS uses mass selective instability; however, this instrument operates at a greater trapping frequency and without a buffer gas. Thus, a useable mass range from 2 to over 50 daltons (Da) is achieved. The performance of the ion trap is evaluated using part-per-million (ppm) concentrations of hydrogen, helium, oxygen, and argon mixed into a nitrogen gas stream, as outlined by the National Aeronautics and Space Administration (NASA), which is interested in monitoring for cryogenic fuel leaks within the Space Shuttle during launch preparations. When quantitating the four analytes, relative accuracy and precision were better than the NASA-required minimum of 10% error and 5% deviation, respectively. Limits of detection were below the NASA requirement of 25-ppm hydrogen and 100-ppm helium; those for oxygen and argon were within the same order of magnitude as the requirements. These results were achieved at a fast data recording rate, and demonstrate the utility of the QITMS as a real-time quantitative monitoring device for permanent gas analysis. (J Am Soc Mass Spectrom 2002, 13, 1120–1128) © 2002 American Society for Mass Spectrometry

When Wolfgang Paul patented the QITMS in 1960, he realized its applicability to analyzing trace components in a sampled atmosphere [1]. However, commercial development of the QITMS occurred decades later with the advent of mass selective instability and use of helium as a collision gas within the ion trap [2–4]. This analyzer environment is unfavorable for trace analysis of hydrogen and helium, and little effort has been made to develop QITMS technology for this purpose.

Historically, there is a precedent for using ion traps with hydrogen and helium in other applications. Dehmelt utilized an ion trap to contain hydrogen [5] and helium [6] ions in separate studies of physical and chemical processes. For these experiments, the ion trap was used exclusively as a storage device without mass analysis. Dawson was the first to report results of

mass-analyzed hydrogen ions with a QITMS [7]. For this work, Dawson's mass selective storage method was used, which involved trapping and detecting ions one mass-to-charge (m/z) value at a time. Compared with mass selective instability, Dawson's method is impractical for performing routine trace analysis of permanent gases because it is complex and time-intensive [3]. Alheit et al. utilized atomic and molecular hydrogen ions when characterizing instabilities associated with higher-order anharmonicities within the ion trap [8–10]. Ions of differing m/z values were simultaneously stored and then removed from the ion trap. Mass analysis was performed using time-of-flight based on the ion's flight time from exiting the ion trap to impinging on an electron multiplier rather than using the ion trap for mass selection.

The mass selective instability method for ion trap mass analysis is utilized on commercial and most research QITMS instruments. Its wide use owes to numerous benefits when compared with other methods. It is time-efficient with a high duty cycle, large dynamic range, and high sensitivity [3, 4] at a reduced

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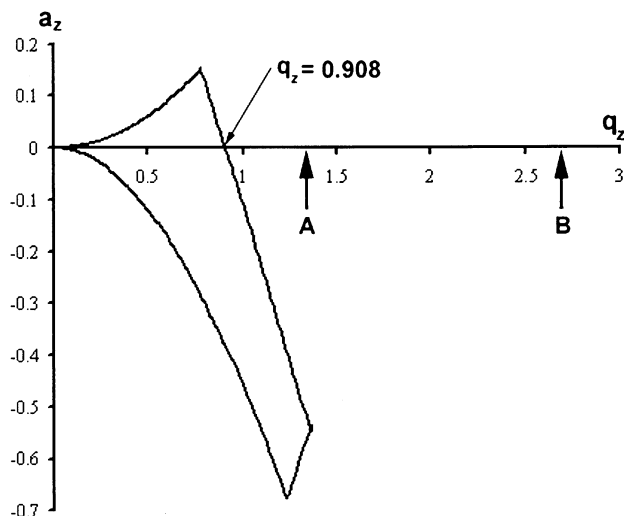


Figure 1. Diagram of the primary stability region in a_z , q_z space. With mass selective instability, ions are positioned along the $a_z = 0$ line and are ejected from the ion trap upon reaching the $\beta_z = 1$ boundary at $q_z = 0.908$. Using a GCQ set to its lowest mass cutoff: a) helium ions are at $q_z = 1.35$; b) hydrogen ions are at $q_z = 2.70$, and are unstable.

cost. The mass range of a QITMS in this mode of operation can be customized through selecting appropriate values for the ion trap dimensions, r_0 and z_0 , and the angular frequency applied to the ring electrode, Ω . These are related through the Mathieu equation, shown in its axial transformed state in Eq 1.

$$m/z = \frac{8V_{RF}}{q_z(r_0^2 + 2z_0^2)\Omega^2} \quad (1)$$

To extend the mass range to thousands of daltons, commercial QITMS instruments utilize ion trap parameters that sacrifice the ability to analyze hydrogen and helium, which lie beyond the stability boundary at $q_z = 0.908$, depicted as (A) for He⁺ and (B) for H₂⁺.

The use of a collision gas, such as helium, further improves the use of the ion trap as a mass spectrometer [2, 3]. These improvements, however, are most noticeable at larger m/z values (i.e., >100 m/z). Use of a collision gas improves performance through collisional dampening of the analyte ions' motion within the ion trap. This process becomes more efficient with increasing mass difference between the analyte and the collision gas species. Hydrogen and helium ions are far too small to benefit from the use of a collision gas. Furthermore, the presence of a low-molecular-weight collision gas, such as helium, would fill the ion trap and saturate the detector when attempting to analyze for hydrogen or helium. Other permanent gases, such as oxygen or argon, also benefit little from the use of a collision gas. Mass resolution is unimproved, and sensitivity is, at most, doubled with use of a collision gas [11].

There are numerous markets (e.g., environmental, industrial, petrochemical, etc.) for performing quantita-

tive analysis of permanent gases. Analysis of hydrogen and helium is more of a niche market; however, both the nuclear and space industries have historically been interested in such an application. NASA, in particular, utilizes mass spectrometers for monitoring the atmosphere within the Space Shuttle for hydrogen and other permanent gases [12, 13]. The potential of QITMS for this application has already been discussed [14, 15], and similar work conducted recently at the Jet Propulsion Laboratory has also confirmed the potential of QITMS operated in the mass selective instability mode for hydrogen and helium analysis [16, 17].

The Space Shuttle main engines consume liquid hydrogen and oxygen. The mass spectrometers used by NASA provide quantitative information to launch controllers, indicating the concentration of hydrogen, helium, oxygen, and argon within nitrogen-purged compartments prior to launch. Hydrogen and oxygen are monitored since they are the cryogenic fuel and oxidizer. Helium is monitored since fuel lines are pressurized with this gas for leak detection prior to cryogenic fueling. Argon is monitored to distinguish between an air leak (0.94 percent argon in air) and a cryogenic oxygen leak.

The effectiveness of these systems, however, is limited by the long delay (>20 seconds) between sampling and analyzing, resulting from the lengthy sample transport lines (>200 feet). To improve flight safety, NASA is interested in miniaturized, rugged mass spectrometers that may be placed close to the Space Shuttle. Though most types of mass analyzers can be miniaturized [18], QITMS is of particular interest to NASA because of its demonstrated high sensitivity when operating with fast update rates. The high duty cycle of the QITMS allows for rapid sampling even when the instrument is miniaturized. When performing real-time monitoring of the internal atmosphere of the Space Shuttle, fast update rates are essential since critical events occur in the last moments prior to launch (e.g., the igniting of the main engines at $t = -6.6$ s).

Considered here is the use of mass selective instability with QITMS for trace analysis of hydrogen and helium, as well as other permanent gases. Conditions necessary for analysis by QITMS over a nominal mass range from 2 to 50 Da are presented, along with performance results including limits of detection, accuracy, precision, response time, and recovery time.

Experimental

QITMS Instrumentation

A compact quadrupole ion trap mass spectrometer was assembled from commercial components fitted into a compact design. The vacuum manifold, ion trap, and filament were selected from a Finnigan (Austin, TX) ITS-40 ion trap mass analyzer, which produced ions within the ion trap volume by electron impact (EI). Low-molecular-weight ions are effectively trapped

when using internal EI, despite the absence of a collision gas. The internal EI assembly is compact and rugged and is suited for use in a miniaturized instrument. The ring-shaped quartz spacers used in the standard ITS-40 ion trap assembly were replaced by ceramic standoffs, which improved response and recovery times by increasing mass flow through the ion trap. The ITS-40 gas chromatograph transfer line assembly was replaced with a 3.5-inch-long stainless-steel transfer tube with a 0.125-inch inner diameter and a 0.125-inch Swagelok external connector. Sample gas delivered through this transfer tube exits between the ring electrode and the exit end cap. A 1-inch NW-16 o-ring-style fitting was added to the vacuum manifold to accommodate a Granville-Phillips (Longmont, CA) model 354 Micro-Ion high-vacuum gauge, which approximately measures the pressure within the open ion trap. A Pfeiffer (Hudson, NH) TPH-065 turbo-drag pump with a TCP-015 control unit was used to produce the high vacuum. Two mechanical pumps were evaluated for backing of the turbo-drag pump: A Vacuubrand (Wertheim, Germany) MZ/2D diaphragm pump noted for its compact and oil-free design and a BOC Edwards (Wilmington, MA) RV3 dual-stage rotary-vane mechanical pump providing lower backing pressures with high compression ratios.

The control electronics from a Finnigan GCQ ion trap mass analyzer offered improved technology over the ITS-40 equivalent. The ion gating circuit of the GCQ controlled the ITS-40 electron gate; the gate is held at +135 volts (V) when ionizing and –130 V when gating electrons. Minor changes to the electron filament circuit of the GCQ electronics were necessary to regulate emission from the ITS-40 filament assembly, which provides 200 microamperes (μA) of 90-electronvolt (eV) electrons. A DeTech (Palmer, MA) model 2312M ceramic electron multiplier, as used in the GCQ, was installed into the ITS-40 manifold to match with the GCQ electrometer circuit; the electron multiplier was held at 1700 V during mass analysis.

Computer control of the instrument was accomplished through customized software developed within the Finnigan Custom Tune Version 1.1 Visual Basic development package, which provides user interface to the underlying C++ code. A module was written for performing real-time monitoring of selected gases at a chosen update rate. For these experiments, an update rate of 1 s was chosen, and m/z values of 2, 4, 32, and 40 were monitored.

RF Circuit Modifications

The commercial instruments used in constructing the customized QITMS (GCQ and ITS-40) each had a low mass cutoff above 4 Da. Without changing the ion trap parameters, the customized QITMS would also have had a low mass cutoff above 4 Da. It is possible to increase the RF amplitude and well depth needed for analysis below m/z 4 by modifying either the angular

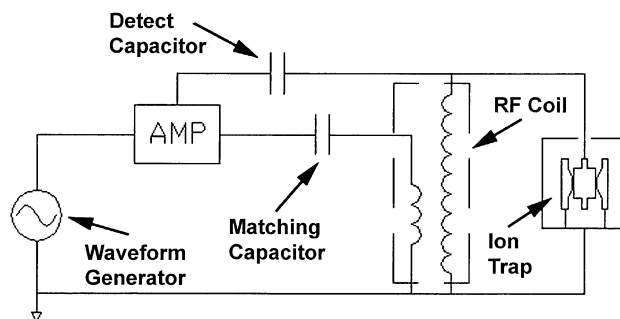


Figure 2. Schematic of RF circuit used to produce the RF trapping frequency. The RF coil and matching capacitor are modified in order to vary the RF trapping frequency.

frequency (Ω) or the ion trap dimensions (r_0 and z_0). Changing the ion trap dimensions, in our case, was unrealistic since the required ion trap size was larger (see Eq 1) than that which could fit inside the vacuum manifold. Even with a new vacuum manifold, it would have been difficult to fabricate multiple hyperbolic ion traps with incremental dimension changes. Changing the RF was more practical, requiring the least amount of modification and fabrication. Increasing RF frequency dramatically reduced mass range, but this was a minor concern here since the desired mass range ended at 50 Da, a 95% reduction from the GCQ upper mass limit.

To increase the angular frequency from that used on the commercial instruments (1 MHz), it was necessary to modify the RF circuitry (see Figure 2). The signal starts at the GCQ waveform generator, which outputs a software-selected frequency up to 5 MHz. On the GCQ, a low-pass filter is then used to clean the signal of higher-frequency distortions. Here the chosen RF frequency is above that used on the GCQ, so the filter board was removed to prevent rejection of the new signal. The waveform then passes through a solid-state amplifier, which worked adequately at frequencies below 3 MHz. An RF coil (an air core transformer) performs the final stage of amplification. The RF coil is part of a resistive, inductive, capacitive (RLC) network, which will only pass signals within a narrow frequency band centered at the resonant frequency. Therefore, a newly selected trapping frequency would have to be at the resonant frequency of the circuit. Three replacement coils were built to provide resonant frequencies between 1 and 4 MHz (see Figure 3). Each of the RF coils had a different radius, providing different ranges of resonant frequencies. Multiple tapping points were placed at increments of a few windings to allow for small changes in the resonant frequency.

Mixing and Delivery of Gas Standards

Standard gas mixtures were used to evaluate the performance of the QITMS. All were mixed in a nitrogen background with a user-defined amount of four analytes: hydrogen, helium, oxygen, and argon. The mixing apparatus, illustrated in Figure 4, was fed by three gas

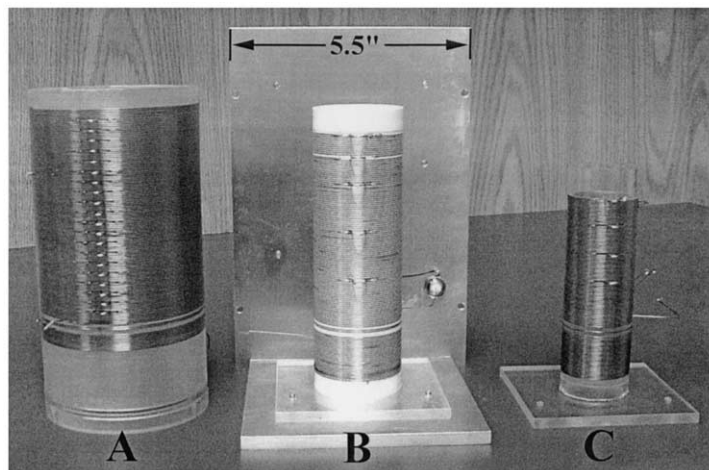


Figure 3. RF coils used to provide the RF trapping field to the ion trap. A range from 1 to 4 MHz is achieved with these coils, each with multiple tapping points: (a) 1.0 to 2.3 MHz, o.d. = 3.48"; (b) 1.9 to 3.1 MHz, o.d. = 1.85"; (c) 2.8 to 3.9 MHz, o.d. = 1.49".

cylinders (BOC Edwards, Wilmington, MA). The first contained 99.9995% nitrogen gas. The second contained the four analytes each at 500 ppm ±5%, balance nitrogen. The third contained the four analytes each at 25,000 ppm ±5%, balance nitrogen. The manufacturer then certified each bottle to a tolerance of ±2%, relative.

MKS (Andover, MA) mass flow controllers (MFC's) were used to regulate gas flow from each cylinder into a plenum (see Figure 4). Both the pure nitrogen and the 500-ppm standard cylinders were regulated through 1000-

standard-cubic-centimeter-per-minute (sccm) 1479A series MFC's. The 25,000-ppm cylinder was regulated by a 100-sccm 1159B series MFC. Based on the usable flow range of the MFC's, mixtures from 2 to 5000 ppm of each analyte in balance nitrogen could be produced. The pressure within the plenum was manually adjusted with a variable leak valve to 900 ± 5 torr, as measured by an MKS 626A series 1000-torr Baratron gauge. The MFC's and Baratron gauge were controlled and monitored through an MKS 647B multi gas controller, which was

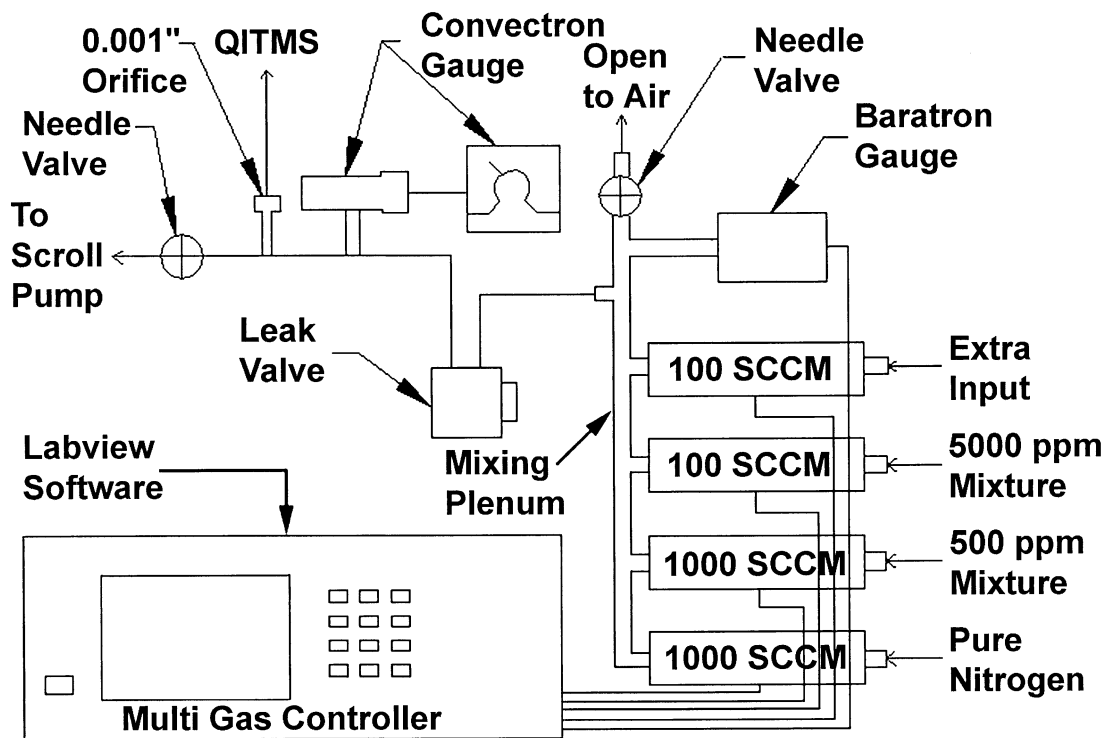


Figure 4. Schematic of gas mixing apparatus and flow-by sample delivery set up. Controlled gas flows are mixed within the plenum (900 torr) from which a lower pressure gas stream (4 torr) is draw by a mechanical pump past the mass spectrometer's sampling orifice.

computer-interfaced. Custom software developed using National Instruments (Austin, TX) LabView 6i permitted rapid switching between desired gas concentrations. Included was a scheduling feature that allowed the user to set up a time sequenced experiment where sample concentrations would automatically change at specified time intervals.

A sample gas stream was drawn from the plenum using a Varian (Lexington, MA) SH-100 oil-free scroll pump through a Granville-Phillips variable leak valve. The stream flowed past a 0.001-inch entrance orifice (O'Keefe Controls Co., Trumbull, CT) attached to the transfer tube leading into the QITMS. A Granville-Phillips type 127 convector gauge measured the pressure in the vicinity of the entrance orifice, while the variable leak valve regulated this pressure at 4 ± 0.25 torr. This differential sampling scheme provided both the higher pressures needed for proper mixing and an acceptable pressure for sampling into the QITMS.

To assess the mixing apparatus, a Stanford Research Systems (Sunnyvale, CA) model RGA 100 quadrupole mass spectrometer was used. NASA has used this unit extensively with the gases of interest. Since the performance of this unit is known, it is suited for comparing the mixing apparatus to the use of discrete fixed concentration gas cylinders. Sample from either of these gas supplies was selectable by a T-valve for delivery into the quadrupole RGA.

Results and Discussion

Examination of Spectral Results after Increasing the RF

Estimating that a trapping frequency between 2 and 3 MHz was necessary to achieve the desired mass range of 2 to 50 Da., coil C (see Figure 3) was installed and tapped for a frequency of 2.8 MHz. At this frequency we first observed an ion signal at m/z 2. To verify the detection of H_2^+ , a test mixture containing 1.25% (each) of hydrogen, helium, oxygen, and argon in nitrogen was sampled. The high gas concentrations were selected because the sensitivity of the QITMS was yet unknown. The results (Figure 5) showed readily identifiable ion signals at m/z 2, 4, 32, and 40, indicating success in achieving a low mass cutoff below 2 Da that would permit the analysis of hydrogen and helium. It was also verified that the upper mass limit was beyond m/z 40, providing a range that included oxygen and argon. The upper mass limit was only a few tenths of a dalton above m/z 40, which accounted for day-to-day difficulties with the argon signal. By switching to coil B and tuning to a trapping frequency of 2.5 MHz, the mass range was increased from 2 up to 60 Da, a preferred configuration.

Having sufficiently reduced the low mass cutoff, the concern now was that the hydrogen background signal (as well as the hydrogen signal in Figure 5) appeared elevated relative to other analyte signals. Hydrogen is

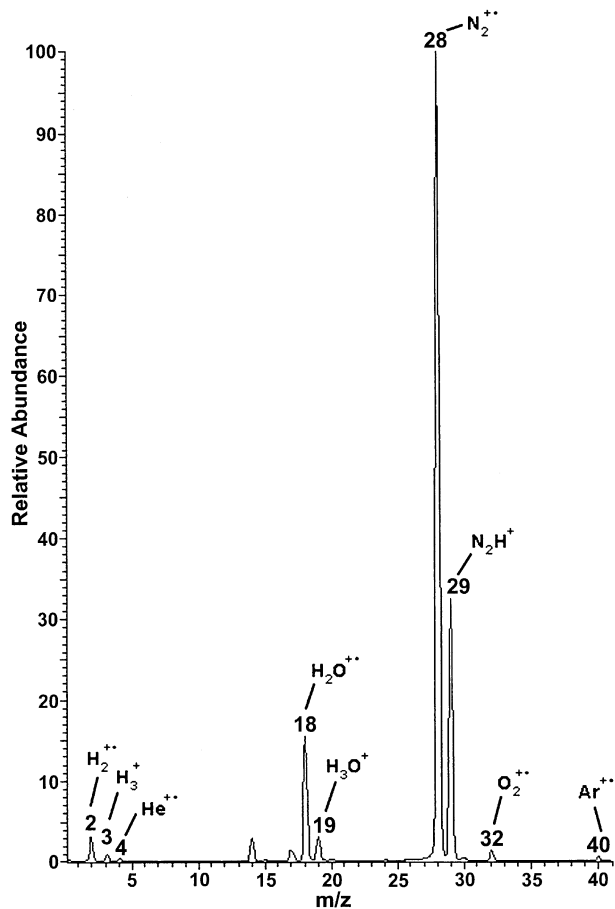


Figure 5. QITMS mass spectrum demonstrating the ability to mass analyze hydrogen, helium, oxygen, and argon, with 1.25% of each in nitrogen being sampled.

known to be the predominant species at ultra-high vacuum levels ($<10^{-8}$ torr) [19], yet at the background pressure of 10^{-6} torr the concentration of oxygen and water should be magnitudes higher than that of hydrogen, not of equal magnitude as the ion signals suggest. It was possible to select ionizing and trapping conditions that preferentially trapped low-molecular-weight species; however, we only observed elevated ion signals for hydrogen and not helium. To further explore this behavior, high-purity nitrogen with 0, 500, and 5000 ppm of hydrogen and helium was analyzed, and the resulting ion signal at each concentration was plotted against time, shown in Figure 6a. After increasing the concentration, the hydrogen ion signal did not reach equilibrium, even after more than an hour. By contrast, helium gave the expected sharp signal increase followed a plateau. When the hydrogen concentration was reduced, the signal decay extended on for hours. A significant hydrogen signal drift observed over 24 h further complicated quantitation of hydrogen.

After adjustments to ionization and trapping parameters failed to improve hydrogen analysis, the pumping efficiency was questioned. The choice of an effective pumping system is not trivial for this application be-

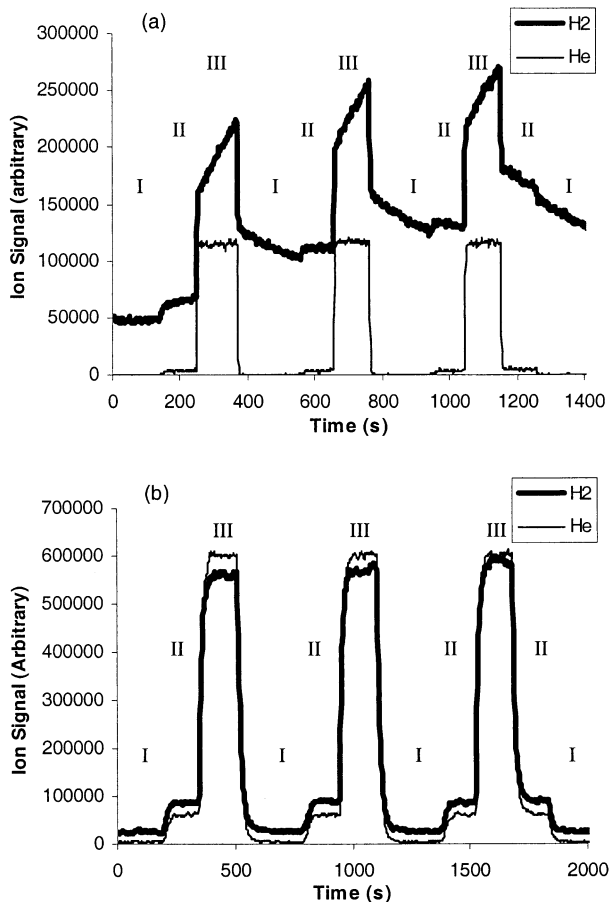


Figure 6. Proper compression of hydrogen from the vacuum chamber is critical: (a) Turbo-drag pump backed by a compact diaphragm pump performed inadequately; (b) turbo-drag pump backed by a dual stage rotary-vane pump demonstrated improved compression ability. (Analyte concentration: I, 0 ppm; II, 500 ppm; III, 5000 ppm.)

cause hydrogen is difficult to pump. Under poor pumping conditions, the hydrogen background would be artificially increased in proportion to other gases. In addition, as extra hydrogen is added, an inefficient pumping system would allow the hydrogen concentration to rise continuously. We replaced the diaphragm pump backing the turbo-drag with a rotary-vane mechanical pump. The results in Figure 6b show that the hydrogen signal now quickly reaches equilibrium when the hydrogen concentration is changed. As well, the hydrogen background signal was reduced by roughly 50%. This illustrates the importance of the pump compression ratios when performing hydrogen analysis.

Another issue associated with hydrogen analysis that is of particular interest with QITMS is protonation. The QITMS traps ions for a minimum of a few ms, sufficient time for any of numerous ion-molecule reactions to become an issue. Protonation within the ion trap is well documented [20]; species having high proton affinities will attach a proton. In our application, those species are hydrogen, water, and nitrogen, all of which are observed in their protonated form in Figure 5

(m/z 3, H₃⁺; m/z 19, H₃O⁺; m/z 29, N₂H⁺). Reaction forming protonated species will end up lessening the amount of H₂⁺ ions available for hydrogen analysis.

Within the monitored Space Shuttle compartments, nitrogen is the bulk component. Because nitrogen is greatly in excess to hydrogen, fluctuations in the amount of nitrogen will play a minimal role on the observed ion signal for hydrogen. Conversely, the concentration of water vapor within the Space Shuttle is more comparable to analyte concentrations. Water vapor within nitrogen-purged compartments can shift noticeably with changing humidity levels outside the Space Shuttle, which may have a significant effect on measured hydrogen concentrations. To evaluate this issue, future experiments will include adding water vapor in a quantitative fashion to gas mixtures and observe the changes in hydrogen ion signal.

In addition to water within the sample, background water in the vacuum chamber can have an important influence on hydrogen sensitivity. Comparing results before and after the vacuum system was baked-out overnight at 125 °C showed that hydrogen sensitivity changed. As expected, baking the vacuum system dramatically reduced the background water vapor detected within the system. The reduced background water concentration resulted in fewer ion-molecule reactions with hydrogen. Subsequently, for the same sample concentration of hydrogen, more hydrogen ions were detected. Baking the vacuum manifold prior to use should prevent such complications.

Evaluating the Gas Mixing Apparatus

NASA has specific evaluation procedures for mass analyzer performance in monitoring hydrogen, helium, oxygen, and argon in nitrogen [21]. Discrete cylinders of each gas at known concentrations serve as the reference standards. To evaluate the QITMS, we have chosen to use a more flexible and versatile gas mixing apparatus (see Figure 4). With the mixing apparatus, a wide range of concentrations is available using a minimal number of gas cylinders. Because our method did not follow the NASA discrete tank process, it was necessary to compare its use with the standard gas delivery method. Both methods produce quaternary gas mixtures in nitrogen.

The gases used as primary standards are rated to a nominal concentration, with the actual concentration in each cylinder certified to within $\pm 2\%$ by the manufacturer. By using a discrete bottle for each concentration, values can deviate by as much as $\pm 4\%$ relative to each other. Historically, NASA has found certified values to be off by more than $\pm 2\%$, which further complicates accurate quantitation. The mixing apparatus requires only two cylinders for these procedures—a quaternary mixture and a cylinder of pure nitrogen. Based on the reported accuracy of the MFC's, error is limited to $< \pm 1\%$. Because the analyte originates from one bottle, values deviate by $< \pm 2\%$ relative to each other, provid-

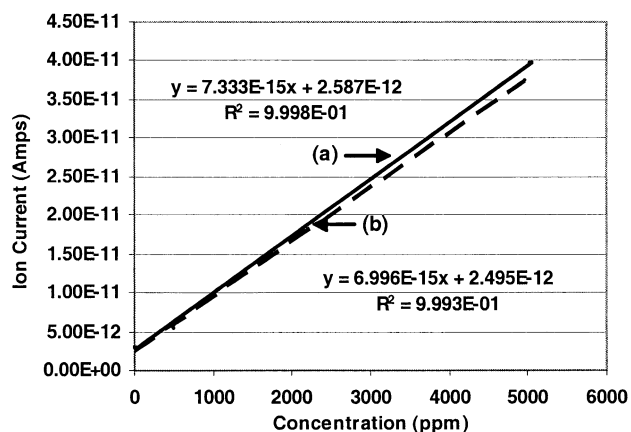


Figure 7. Determination of gas mixing apparatus performance: (a) Hydrogen data collected using gas samples from discrete cylinders; (b) hydrogen data collected using the gas mixing apparatus.

ing for more accurate calibration than with discrete bottles.

Gas samples were analyzed from the discrete cylinders and the gas mixing apparatus to compare their performance. We chose to perform the analysis on a quadrupole RGA that has been well characterized for use with these gases. Mixtures of hydrogen, helium, oxygen, and argon at 0, 500, and 5000 ppm were analyzed sequentially, first from the discrete bottles and then from the mixing apparatus. This was repeated three times, and the data were averaged. The results did not reveal any prominent differences between the two methods. Data from repetitive runs fell within 5% of one another, demonstrating similar precision for each method. The hydrogen data shown in Figure 7 shows a difference in sensitivity of 4.1%. Sensitivity differences for the other gases ranged from 0.5% for helium to 8.0% for oxygen. Results collected from the mixing gas apparatus showed similar linearity compared with the discrete bottle method, with R^2 values all greater than 0.990. Background gas concentrations (Y intercept) varied somewhat, which may be because different pure nitrogen bottles were used for each, although a certain amount of background drift was expected. In all, the performance of the mixing apparatus is comparable to the discrete bottle method, while being more flexible for experiments, producing concentrations throughout the range from 2 to 5000 ppm.

Results of QITMS Performance Evaluation

The countdown to a Space Shuttle launch involves an intricate series of events spanning more than 72 h. Leak-detecting mass spectrometers are first activated 48 h prior to liftoff. Each mass spectrometer is calibrated and tested for accuracy, precision, and limits of detection. Once launch controllers have determined that the mass spectrometers meet all requirements, the units are put online for monitoring key regions inside the Space

Table 1. NASA-required performance specifications

Performance criteria	Basic requirements ^a
Accuracy (% error)	<10% or 5 ppm, whichever is less
Precision (% deviation)	<5% or 3 ppm, whichever is greater
Detection limit (ppm)	H ₂ : 25; He: 100; O ₂ : 25; Ar: 10
Response time (sec)	10 (0 ppm raised to 500 ppm)
Recovery time (sec)	30 (500 ppm lowered to 0 ppm)

^aRequirement for all gases, unless otherwise stated.

Shuttle. NASA has outlined similar calibration and testing routines for evaluating new mass spectrometer technologies such as the QITMS reported here. Tested are accuracy, precision, and detection limits, as well as response and recovery times. Table 1 outlines the NASA requirements in each performance category.

Evaluation results for the QITMS are reported in Table 2. The accuracy and precision for each gas are below the requirements stated in Table 1. The most accurate and precise data were measured for helium. The superior performance for helium results from the low background, both internal and external, to the mass spectrometer. Background sources do exist for the other three gases. Stainless-steel vacuum chambers outgas hydrogen, typically noted under high-vacuum conditions. Oxygen and argon are potential contaminants, being the second and third most abundant components in air. Helium is neither abundant in the air nor found to outgas under vacuum conditions. Thus, the helium background signal is particularly low with a minimum of signal drift when compared with the other three gases. Reduced short-term drift improves accuracy within each run, while minimized long-term drift keeps the measurements precise and reproducible.

The calculated limits of detection are based on the signal-to-noise ratio measured when sampling pure nitrogen and are influenced by both background fluctuations and sensitivities. The limit of detection for helium is notably worse than that of hydrogen despite the lower helium background. This is likely a consequence of the hydrogen sensitivity being nearly twice that for helium. Though oxygen and argon sensitivities are nearly identical, the limit of detection for oxygen is considerably higher than for argon. The oxygen background was significantly higher, possibly because air diffused into the gas delivery system through the vent valve vent of the plenum (which is open to air, see Figure 4). However, no leak was detected when placing a helium gas stream into the vent valve. Although

Table 2. QITMS performance results

Performance criteria	H ₂	He	O ₂	Ar
Accuracy (% error)	6.9	0.3	6.3	8.2
Precision (% deviation)	2.0	1.3	3.1	4.4
Limit of detection (ppm)	12.0	17.5	33.1	19.3
Response time (seconds)	8.0	7.0	8.0	8.0
Recovery time (seconds)	6.0	6.0	8.0	6.0

helium, oxygen, and argon diffuse differently, the helium leak check suggests that an air leak is improbable. More likely, charge-exchange may be exaggerating the background signal for oxygen. Oxygen has the lowest ionization energy of the analytes and is preferentially ionized by charge-exchange—notably with increased time within the ion trap. The limit of detection for argon was also above NASA requirement. This is attributable to the requirement for argon being the strictest of the four. For the instrument optimization should improve the limits of detection for both oxygen and argon.

A plus for the QITMS is its speed—faster than the NASA requirements—resulting from its high duty cycle in which each data point is an average of 120 scans. Data are displayed and stored every second—six times faster than other MS systems currently used on the launch pad [12, 13]. Though quantitative results are often a trade-off for speed, the QITMS has demonstrated that, even with the update rate of 1 Hz, adequate quantitative results are achieved.

Besides a quick update rate, it is important that the instrument responds and recovers quickly to changing analyte concentrations. NASA is interested in the response and recovery time needed to reach 95% of equilibrium when switching gas loads from 0 to 500 ppm and from 500 to 0 ppm, respectively. Eight instruments were evaluated as complete systems (includes: sample transport, ionization, mass analysis, pumping, and detection). A common sample delivery method was employed up until the mass spectrometer inlet (one exception required a different inlet pressure), along with similarly sized vacuum pumps. By measuring the period from the start of the ion signal change rather than from the moment the gas was switched, disparities resulting from the use of different inlet designs were diminished. Table 2 shows that for all four gases the QITMS responds and recovers quicker than the respective 10- and 30-s requirements listed in Table 1. The QITMS is one of only two systems capable of responding within 10 s, and is the only one of the group able to recover within the prescribed time [21]. In part, this performance is the result of the open source design of the QITMS, which allows for quicker replacement of the gas volume than with a closed source design.

Conclusions

Presented is an ion trap instrument utilized in the mass selective instability mode for mass analysis without the use of a buffer gas. Using an RF trapping frequency of 2.5 MHz, the customized QITMS operates over a mass range of 2 to 60 Da. The instrument performs well when quantitating hydrogen, helium, oxygen, and argon in a nitrogen background. Accuracy and precision are better than $\pm 10\%$ and $\pm 5\%$, respectively, and limits of detection are at low ppm levels. The QITMS operates at a fast update rate, with quick response and recovery when

exposed to changing concentrations. Future drift tests are needed to determine the stability of the instrument over long periods. Variations in humidity, temperature, and pressure will need to be examined for their effects on background levels and sensitivity. All criteria are within NASA specifications required to support Shuttle launch operations, except two marginally high limits of detection, which should be remedied through future optimization. Moreover, the quick performance of the customized QITMS makes it particularly suited to monitoring for cryogenic fuel leaks in the final moments prior to liftoff of the Space Shuttle.

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