Optimizing Quadrupole Performance When Coupled With High Voltage Ion Sources

Richard A. Schaeffer
Extrel CMS LLC, 575 Epsilon Drive, Pittsburgh, PA 15238

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Some applications require the ion birth potential to be elevated far from ground. In these cases, the quadrupole pole bias must be elevated far from ground to allow for reasonable quadrupole ion energies, but most system designs have a grounded quadrupole housing.

Problem: When operating with quadrupole pole bias different from quadrupole housing potential, poor performance results.

- Sensitivity can diminish by more than an order of magnitude.
- The housing potential asserts itself into the quadrupole field yielding split mass peaks due to octupolar and dodecapolar non-linear resonances.

Solution: These effects can be avoided by electrical isolation of the quadrupole housing, with the housing potential maintained within ten to twenty volts of the pole bias.

I. INTRODUCTION

Quadrupole performance is generally optimum when the ion energy through the quadrupole is limited to five or ten eV. At higher ion energies, abundance sensitivity, resolution and peak shape suffer. In certain applications it is inconvenient or impossible to force the potential at which the ions are born to be at or near ground. Examples of such applications are SIMS, hybrid MS/MS instruments (BEqQ), plasma monitoring, flow tubes, and other specialized ion sources. One is therefore given the choice of settling for non-optimum quadrupole performance, or floating the quadrupole pole bias to within five or ten volts of the ion region potential.

Quadrupoles are typically mounted inside a grounded cylindrical housing. If the pole bias differs more than twenty volts from the quadrupole housing potential, peak splitting due to even order non-linear resonances is evident in the spectra.

This presentation includes an experimental and theoretical treatment of the problems associated with optimizing quadrupole performance when the ion source potential is by necessity elevated far from ground.

II. EXPERIMENTAL

A standard Extrel 9.5 mm quadrupole probe with 041-11 Axial Molecular Beam Ionizer and counting electron multiplier was modified to allow electrical isolation of the multiplier housing. This isolation was effected by the addition of a Vespel (polyamide) insulator between the quadrupole exit lens mounting hardware and the multiplier housing. The quadrupole exit lens was modified by the addition of a short tube lens, which penetrates into the multiplier housing. (Note: This design has been modified in production units to use vacuum compatible Alumina Insulators in place of the Vespel.)

The bias potential was applied to the circuit common connectors at the back of the Extranuclear Labs (ABB Extrel) 020-2 ionizer control electronics, 0-11 QPS quadrupole power supplies with Model 15 High Q Head, to the Faraday aperture plate and to the quadrupole housing. See Figure 1 for a schematic representation of the physical modifications and electrical connections.

The tune voltages were: Ion Region, +5; Extraction Lens, -1; Lens 1 and 3, -19; Lens 2, -153; Quadrupole Entrance Lens, 0; and Quadrupole Exit Lens, -2 Volts. Pole Bias was set to 0 Volts, with 1.7 kV applied across the Multiplier and the Dynode grounded. A bias voltage was summed with all of these voltages through the electrical common of the control electronics. The quadrupole housing was alternately

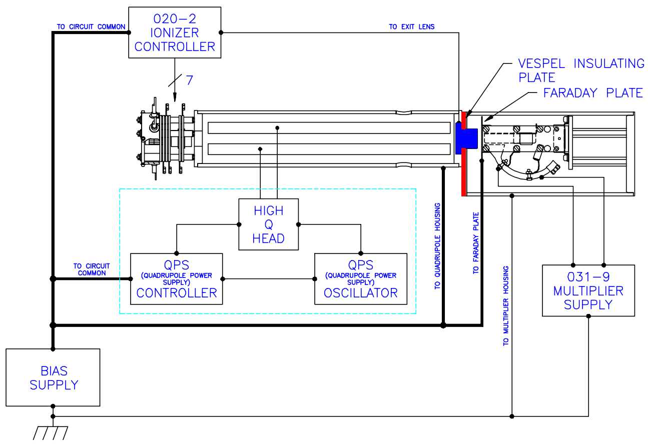

Figure 1. Schematic of Extrel Quadrupole probe assembly with electrically isolated quadrupole housing and electrically biased control electronics. Modifications from standard design include the addition of a vespel insulating plate between the multiplier housing and quadrupole housing, and a modified exit lens design.

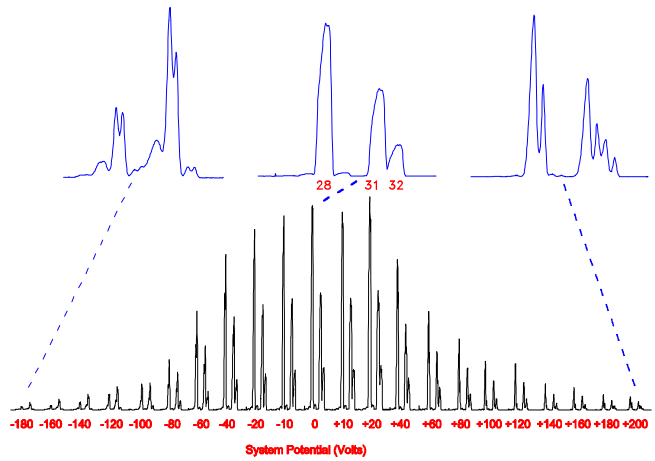

Figure 2. Quadrupole peak shapes with grounded quadrupole housing and biased control electronics.

grounded or biased using this bias voltage in these experiments.

III. FLOATING THE QUADRUPOLE WITH GROUNDED HOUSING

When ionizer and quadrupole pole bias are floated from ground, but the housing is grounded, quadrupole performance is adversely affected.

In the spectra of masses 27 to 33 (m/z 28 and 32 from an air leak, m/z 31 from perfluorotributylamine) shown in Figure 2, one can see that absolute sensitivity drops rapidly as the pole bias differs from the housing potential by more than twenty volts. Indeed, with a two hundred volt positive or negative potential difference, the sensitivity of the analyzer drops by a factor of twenty.

Peak shape changes dramatically as well, yielding characteristic peak splitting and broadening. The relative intensities of the various mass peaks distort as well, with m/z 28 relative intensity reduced with increasingly negative voltage deltas.

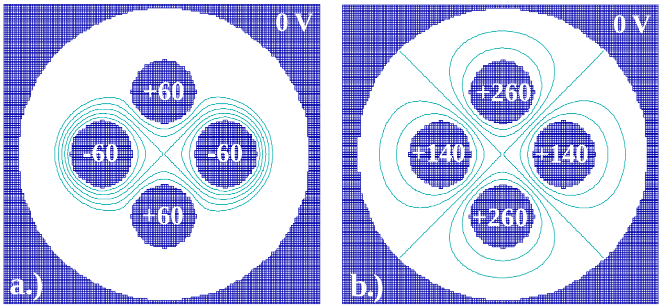

Figure 3. Equipotential contours for a quadrupole with grounded housing: a.) 0 Volt pole bias. b.) 200 Volt pole bias.

IV. WHAT CAUSES THIS PEAK SPLITTING?

Dennison [1] demonstrated that the grounded field of a

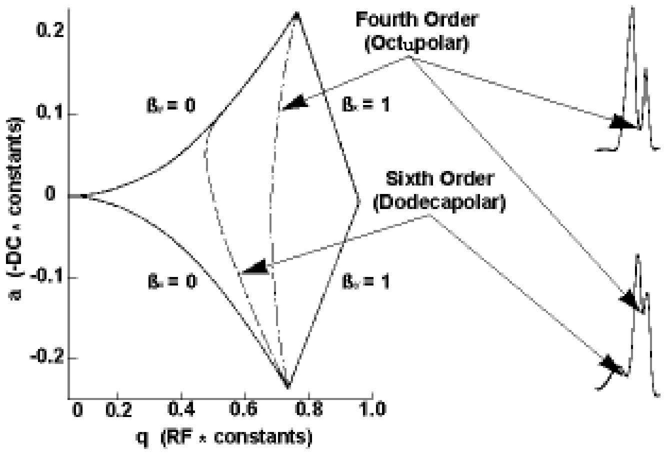

Figure 4. Mathieu stability diagram showing characteristic octupolar and dodecapolar non-linear resonance lines. These non-linear resonance lines correlate well with experimental peak shapes shown. Adapted from Reference 2.

Extrel CMS LLC
575 Epsilon Drive • Pittsburgh, Pennsylvania 15238-2838 USA
Phone: (412) 963-7530 • Fax: (412) 963-6578 • Web: www.extrel.com • E-mail: info@extrel.com

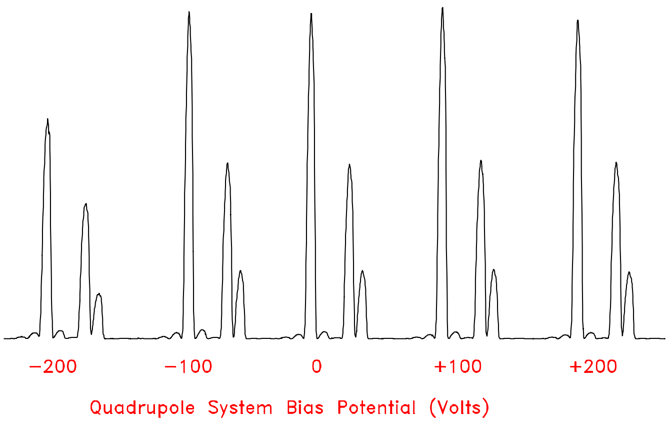

Figure 5. Quadrupole peak shapes with biased quadrupole housing and control electronics.

quadrupole housing alters the effective radius of the quadrupole rods, even when the pole bias matches the housing potential. When the housing potential differs greatly from the pole bias, the housing potential penetration into the quadrupolar field is more dramatic, yielding octupolar and dodecapolar field distortions

Figure 3 illustrates the magnitude of these field distortions. Note the differences in the shapes of the equipotential contours between grounded and -200 V housing potentials.

The effects of such field distortions were calculated theoretically by Dawson in 1972 [2]. In this work, Dawson correlated fourth order (octupolar) and sixth order (dodecapolar) field distortions with split peaks.

The Mathieu stability diagram in figure 4 is adapted from Reference 2. The peak splitting evident in the spectra can be rationalized as follows: When the housing potential is more positive than the pole bias, as is the case of a negative system potential and grounded housing, the negative DC voltage offset corresponds to a positive Mathieu 'a' parameter, with peak splitting characteristic of the upper half of the stability diagram, namely octupolar peak splitting. For the case of the housing potential more negative than the pole bias (positive system potential), the peak splitting is characteristic of the negative 'a', bottom half of the stability diagram, with peak splitting attributed to both octupolar (split top) and dodecapolar (pre-cursor with peak broadening) field distortions.

V. FLOATING BOTH THE QUADRUPOLE AND HOUSING

If the housing potential is maintained at the same bias potential which elevates the rest of the analyzer, analyzer performance returns to normal levels, independent of bias potential.

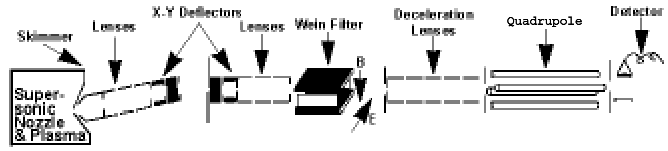

Figure 6. The Johns Hopkins Anion Cluster Analysis System.

From Figure 5, it can be seen that the non-linear resonance effects are eliminated through the elevation of the housing potential, with no loss in sensitivity as the bias potential goes to more and more positive voltages.

When the bias potential is elevated to more negative potentials, a slight reduction in sensitivity is evident, which is attributed to a reduction in detection efficiency. Since detection efficiency is dependent on the acceleration of ions exiting the quadrupole to an off-axis detector, a reduction in the acceleration potentials results in both a reduction in ion energy as the ion strikes the multiplier surface and a slight change of the focusing of the ions into the multiplier cone. Both of these effects contribute to a loss in sensitivity as the voltages are changed from optimum values.

These effects can be eliminated by biasing the multiplier and dynode supplies similar to the biasing of the ionizer and quadrupole supplies, and the use of a high voltage on the conversion dynode.

VI. TYPICAL APPLICATION: SAMPLING A PLASMA

A typical application where the quadrupole pole bias must be floated from ground is shown in Figure 6. This system for the characterization of negative ion clusters is in use by the Bowen group at the Johns Hopkins University in Baltimore, Maryland.

This system was designed to allow sampling of a plasma. As the plasma potential is brought closer and closer to ground, the absolute sensitivity of the system suffers. In order to maintain instrument sensitivity, the plasma potential must be maintained at a potential far from ground. It is therefore necessary to elevate the bias potential of the quadrupole system to within ten volts of the potential of the plasma to yield optimal quadrupole performance.

The objective of this experiment is to use a mass spectrometer to probe the physical characteristics of clusters. Mass spectra of these clusters indicate unusual stability's by the appearance of 'magic numbers', a cluster size that is

Extrel CMS LLC
575 Epsilon Drive • Pittsburgh, Pennsylvania 15238-2838 USA
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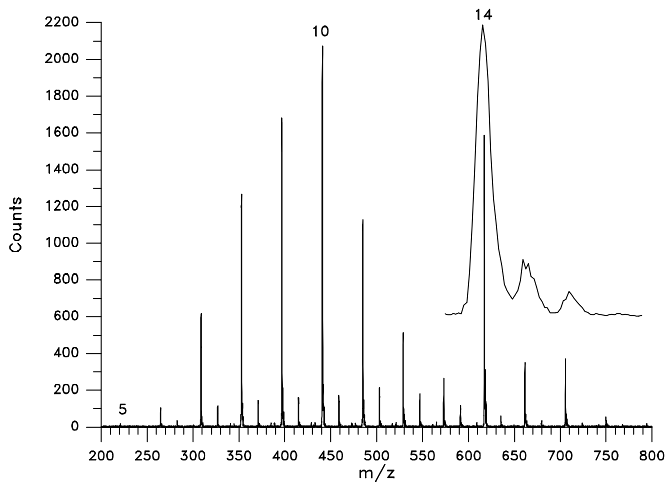

Figure 7. Typical CO_2 anion cluster spectrum from Johns Hopkins system. Quadrupole mass analyzer and control electronics were isolated -390 Volts from ground. Labels indicate number of CO_2 atoms in cluster. Inset illustrates excellent peak shape for $(CO_2)_{14}$.

followed by a sharp decrease in intensity of the next size. Magic number clusters are then explained in terms of their geometric and electronic structure.

In this experiment, a supersonic nozzle is used to inject carbon dioxide clusters into a weakly ionizing plasma (-400 Volt plasma potential). Anion clusters are extracted and collimated from this plasma. The ion beam is extracted off-axis from the quadrupole center-line to eliminate line of sight between the plasma and the detector, with X-Y deflectors used to steer the ions into the analyzer. The ions then go through a Wien velocity filter, which can be tuned either to pass all ions, or to serve as a mass filter to separate a narrow range of ions from the monoenergetic ion source for photofragmentation, with subsequent mass analysis of the fragments using the quadrupole mass filter. These high energy (400eV) clusters are decelerated to 10-15eV before entering an Extrel quadrupole mass filter, which is biased -390 Volts from ground. This biasing is effected using the scheme identified in figure 1.

VII. CONCLUSIONS AND FUTURE WORK

This presentation identifies the symptoms and source of some of the problems associated with analyzing ions whose birth potential is elevated far from ground, specifically poor peak shape and sensitivity. By biasing the potential of the complete analyzer including the quadrupole housing, these problems can be minimized.

In these data, the dynode potential was maintained at zero volts to emphasize the importance of the bias potential on detection efficiency. Maintaining the dynode potential at 5000 Volts from ground should minimize this effect.

This work was performed using vintage vacuum tube electronics, which has a maximum bias offset of 400 Volts. Similar results can be obtained using current vintage solid state electronics, with the integral pole bias offset limited to the 200 Volt internal pole bias supply.

For isolation of the mass analyzer to extreme voltages, (thousands to tens of thousands of Volts), as required for a hybrid BEqQ instrument, a Faraday cage is used electrically isolate the electronics, with the bias potential applied through an isolation transformer which provides the primary system power.

REFERENCES

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2) Dawson, P, Whetten, N.R.; Non-Linear Resonances in Quadrupole Mass Spectrometers due to Imperfect Fields. II. The Quadrupole Mass Filter and the Monopole Mass Spectrometer. Int. J. Mass Spec. Ion Phys., 1969, 3, 1-12.

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