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Optimizing Quadrupole Transmission for Wide Mass Range to 10,000 amu

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The current research focus in clusters characterization and materials science as well as biochemistry has lead to a requirement for increased analyzer mass range. New ionization schemes such as electrospray and various cluster sources have overcome the obstacles of ionizing heavier species and bringing them into the gas phase as ions. The challenge for quadrupole analyzer design is the relationship between mass range and voltage, frequency, transmission and analyzer size requirements. Mass range of a quadrupole system is proportional to applied voltage, and inversely proportional to rod diameter squared and frequency squared. Therefore, one could increase the mass range of a given system by increasing the applied voltage, or reducing the rod diameter and or frequency. This presentation will review the results of our characterization of the key figures of merit for a commercially available quadrupole system with mass range extending to 10,000 amu, constructed of 6 mm diameter quadrupole rods operated at 880 kHz. Also included is a summary of practical hints for maximizing performance at high mass, along with a theoretical treatment examining ion energy and tuning requirements.

I. INTRODUCTION

In this presentation, we characterize the performance for a quadrupole mass spectrometer with 10,000 amu mass range.

The target applications for such a wide mass range include analysis of bio-molecules (peptides and proteins) and clusters of molecules (often loosely bound) for deposition onto a surface.

Recent advances in time of flight technology have revolutionized the analysis of peptides and proteins with high sensitivity, wide mass range, and excellent mass accuracy.

The one challenge that remains difficult for Time-of-Flight mass spectrometers is the ability to selectively deposit a narrow range of masses onto a surface for subsequent analysis by some other technique.

Optimal deposition experiments require a constant current of a narrow mass range at low ion energy (a few eV or less). Time-of-Flight systems typically have pulsed ionization, and have high ion energies that preclude gentle deposition.

It is common knowledge that quadrupole transmission reduces with increasing resolution. At the 1998 ASMS conference [1], we presented our studies of relative transmission as a function of mass, showing a slight reduction in relative transmission with increasing mass on a given system. Relative transmission at unit mass resolution (~1 amu wide mass peaks) was ~25% to 30% for mass 502 for a 2,000 amu mass range system with pre- and post-filters, and was ~10-15% without pre-and post-filters.

Cluster analysis does not typically require unit mass resolution, rather, the requirement is for a minimum mass resolution suitable to resolve adjacent clusters. For example, if one were looking at water clusters, then the peak width could approach the mass of a single water molecule or 18 amu.

The mass filter in this presentation demonstrates near unity transmission with such broad peaks, making it ideally suitable for cluster deposition experiments.

II. EXPERIMENTAL

The 10,000 amu mass range quadrupole system used in this experiment was constructed from the following components:

- Cesium ion gun with cesium iodide target.
- Axial molecular beam ionizer
- 6 mm tri-filter quadrupole (6 mm rods with pre- and post-filters)
- Electron multiplier detector
- Analog preamplifier

- 0.88 MHz RF power supply with peak voltage of 3800 V, and +/- 200 V pole bias control range
- Extrel Merlin control electronics and data acquisition system configured with seven lens supplies

The quadrupole pole bias was programmed such that its voltage became more and more negative with increasing mass, effectively programming ion energy linear with mass. The pole bias was set to –10 V at 0 amu and was linearly mass programmed to –200 V at m/z 10,000 amu.

The lens supply that biased the entrance lens and pre- and post-filters was programmed such that its voltage became more and more negative with increasing mass, following the pole bias.

A single lens supply was used to drive these three elements simultaneously after it was experimentally determined that they tend to optimize at the same voltages, approximately 20 volts more negative than the pole bias potential.

The cesium iodide target in this system was placed just outside the axial molecular beam ionizer, with the desorbed clusters traveling along the axis of the quadrupole with an unfortunate consequence of having a high number of fast moving ions and neutrals elevating the baseline, especially at low mass.

System mass resolution was slightly over-resolved at lower masses (below 2000 amu) to reduce their intensities in order to enhance the scaling to show the signals for the higher mass ions.

Peak widths could be resolved to as narrow as 2-5 amu across the mass range with dramatic loss in sensitivity.

III. MASS RANGE EXTENSION THEORY

System mass range is proportional to the inverse of square of the rod diameter, and the inverse of the square of the RF frequency. In order to increase the mass range of a system, either the rod diameter or the RF frequency or both would need to be reduced.

Decreasing the frequency of a 2000 amu system from 1.2 MHz to 0.88 MHz yields approximately a factor of two increase in mass range to 4000 amu (using 9.5 mm diameter round quadrupole rods).

Deceasing rod diameter from a 4000 amu 9.5 mm quadrupole to 6 mm diameter yields a 2.5-fold increase in mass range to 10,000 amu.

Reduction in the rod diameter is predicted to reduce absolute transmission by approximately the square of the ratio of the diameters (2). i.e. a 6 mm quadrupole should have ~40% of the transmission of a 9.5 mm quadrupole (6 x 6 / 9.5 x 9.5).

Reduction in RF frequency is predicted to absolute transmission by a fraction somewhat less than the ratio of the two frequencies (assuming a narrow angular emittance of the ion source, increasing angular aceptance of the quadrupole won’t have a very dramatic increase in transmission). Reduction from 1.2 MHz to 0.88 MHz results in a 25-30% reduction in transmission.

IV. ION KINETIC ENERGY FOR HEAVY IONS

One of the key experimental parameters to consider for optimum mass analysis of heavy ions is ion kinetic energy, the energy that the ions have as they travel through the quadrupole.

Optimal ion energy for light ions (1-500 amu) transmitting through a quadrupole is in the range of 5-10 eV. Optimal quadrupole performance tends to go with constant transit time through the quadrupole.

The simple physics equation $E = \frac{1}{2} mv^2$ describes the calculation from energy into velocity.

In order to maintain constant transit time across the mass range, velocity must be constant across the mass range, thus requiring ion energy (pole bias) to be programmed linearly with mass.

If the optimum kinetic energy (pole bias) for m/z 500 is 10 eV, then the optimum pole bias for m/z 10,000 would be 200 eV (twenty times as high an energy for the twenty-fold increase in mass). Indeed, when pole bias is set to 10 eV ion energy across the mass range, the spectrum shown in Figure 1 would be void of signal above mass 1500.

V. QUADRUPOLE TRANSMISSION

A key figure of merit for a quadrupole system used in cluster deposition is the transmission of the quadrupole.

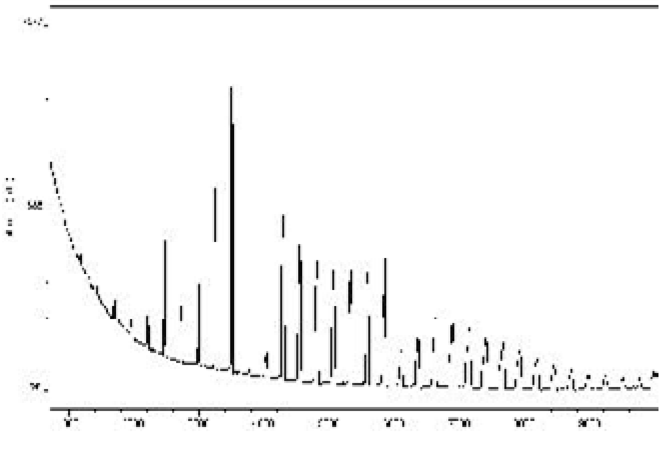

Figure 1. Cesium Iodide Clusters, 700 to 10,000 amu.

Table 1. Relative Transmission as a function of mass range and quadrupole type. *Note that the power supplies for the 19 mm quadrupoles were modified to extend their maximum mass slightly beyond their rated value of 500 amu.*

Quadrupole Type	RF Frequency	Maximum Mass (amu)	Typical Relative Transmission at m/z 502
19 mm tri-filter	1.2 MHz	500	60% – 70%
19 mm standard	1.2 MHz	500	25% - 30%
9.5 mm tri-filter	1.2 MHz	2,000	25% - 30%
9.5 mm standard	1.2 MHz	2,000	10% - 15%
9.5 mm tri-filter	0.88 MHz	4,000	20% – 25%
9.5 mm standard	0.88 MHz	4,000	7% - 10%
6 mm tri-filter	0.88 MHz	10,000	3% - 4%

Quadrupole transmission can be measured as the intensity of ion current at the required resolution divided by the intensity of ion current when the quadrupole resolution is opened up such that additional increase in peak width results in no increase in intensity.

The relative transmission of the cesium iodide clusters shown in Figure 1 at the resolution shown is near unity; opening up the resolution results in wider peaks but the amplitude does not increase significantly.

The relative transmission of various other quadrupole configurations is shown in Table 1.

Absolute transmission (mA of ion current to the detector as a function of partial pressure of gas) tends to closely follow relative transmission for light weight gaseous species. Since it is difficult to generate measurable partial pressures of higher molecular weight species, absolute transmissions must be estimated by relative transmissions.

VI. CONCLUSIONS AND FUTURE WORK

This work demonstrates the performance of a 10,000 amu mass range quadrupole system suitable for deposition of clusters onto a surface.

The relative transmission of the 6 mm quadrupole tested was about half that predicted based on the reduction in rod diameter from a 9.5 mm quadrupole. It is believed that the average performance of production 6 mm quadrupoles might be better than seen for the prototypes.

Key to achieving suitable performance are the requirement to program the pole bias potential with mass to program ion energy with increasing mass.

The system will be further characterized to focus on the following attributes:

- Transmission as a function of mass resolution.
- Ultimate resolving power as a function of mass.
- Effect of housing bias potential on peak shape and transmission.
- Abundance sensitivity across the mass range.

REFERENCES

(1) Pedder, R.E., Wei, J. “Quadrupole Performance: Do Quadrupoles Discriminate Against High Masses?” *Presented at the 46th ASMS Conference on Mass Spectrometery and Allied Topics, Orlando, Florida, June 4, 1998.*