Practical Quadrupole Theory: Miniaturization of Rod Diameter, Length, and Frequency

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There are a number of parameters which control quadrupole mass range and transmission, including rod diameter, RF frequency and rod length. With the trend toward miniaturization of analyzers, it is becoming increasingly important to minimize power and size requirements. The question is how small is too small? Mass resolution is very much dependent upon RF frequency, rod length and the energy of the ions as they transmit through the quadrupole. Mass range and voltage requirements are inversely proportional to both the square of rod diameter and the square of RF frequency. The fundamental question is whether an increase in RF frequency can offset the performance loss associated with a reduction in rod diameter. In this work, it was determined that for cases where the emissivive area of the ion source is much larger than the acceptance of the quadrupole, absolute transmission is approximately proportional to the square of RF frequency, and the cube of rod diameter.

I. OVERVIEW

The objective of creating portable gas analyzers has lead to a number of efforts to reduce the size of mass spectrometers, including quadrupoles. The objective of this work is to determine the magnitude of performance reduction to be expected by reducing rod diameter.

It is generally accepted that the absolute transmission of a quadrupole mass filter increases with increasing frequency and increases with increasing rod diameter. In this work the relative performance of a number of combinations of quadrupole rod diameter and RF frequency are compared.

Quadrupoles with five different rod diameters (4, 6, 9, 12, and 20 mm), and six RF frequencies (0.88 MHz, 1.2 MHz, 1.44 MHz, 1.7 MHz, 2.1 MHz, and 2.8 MHz) were used in this work.

It was determined that absolute transmission is more strongly dependent on rod diameter (transmission proportional to rod diameter cubed) than on RF frequency (transmission proportional to frequency squared).

II. EXPERIMENTAL

A flange mounted mass filter assembly was assembled as described in table 1.

The quadrupole mass filters consist of four precisely manufactured round parallel rods, suspended around a center axis by two ceramic collars. Figure shows photograph of the 4 mm quadrupole.

The quadrupole mass filter is situated inside a stainless steel or aluminum housing, to which an entrance and exit lens assembly are mounted.

The entrance and exit lens apertures are defined to be just under the inscribed diameter of the quadrupole.

Data was acquired using an Extrel CMS Merlin Automation data acquisition system.

Six different RF power supply frequencies were used as identified in table 2.

These power supplies were brought into resonance with the various quadrupoles through a combination of changing cable lengths, adding makeup capacitance inside the vacuum chamber, and using the variable resonating capacitors built into each of the RF power supplies.

Argon was selected as the test gas species because it is almost mono-isotopic (its isotopes have very low relative abundances). By reducing the electron energy to 50 electron volts, the relative intensity of the doubly charged argon mass peak at m/z 20 was reduced.

A constant partial pressure of 5 X 10^{-5} torr of argon was maintained in the chamber background, to ensure that argon was in far excess, compared to the chamber background, yielding a single m/z value emitting from the ion source. See figure 2 for a typical spectrum.

Table 1. Flange Mounted Mass Filter Configuration:

Component	Description
Flange	8 inch conflat flange with electrical feedthrus
Detector	Continuous Dynode Electron Multiplier with Faraday Aperture Plate, with Faraday ion currents Measured on the Faraday Aperture Plate.
Quadrupole	8 inch long quadrupole mass filter, with 6, 9, 12, and 20 mm rod diameters, and a 4-inch long quadrupole mass filter with 4 mm rod diameter.
Ion source	Axial Molecular Beam Ionizer
	Four coiled tungsten filaments surrounding an
	0.375 inch diameter gold plated molybdenum ion region basket, with
	0.125 inch aperture diameter extraction lens,
	Followed by an einzel lens.

Data acquisition was delayed after each pumpdown, until the chamber background pressure was below 2 X 10^{-6} torr, to minimize the contribution of chamber background to the measured results.

The ionizer was tuned to yield reasonable peak shapes at the lowest RF frequency, exhibiting smooth mass peaks without fine structure. Ion energy was thus maintained at 6 eV for all eight-inch long quadrupole experiments (6 Volt ion region potential, 0 volt quadrupole pole bias), and 3 eV for the four-inch long four-millimeter rod diameter quadrupole.

Electron emission current was maintained at 0.3 mA to minimize effects of electron space charge in the ion source as a source of error.

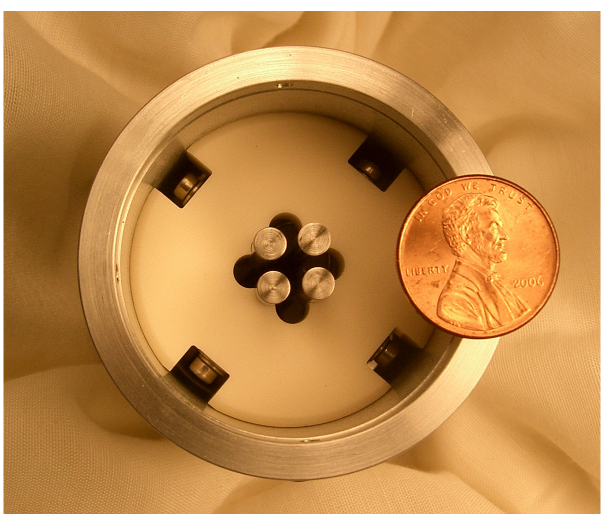

Figure 1. End view of four-millimeter quadrupole.

***Table 2. RF Power Supplies Used in These Experiments*:**

Frequency	Description
0.88 MHz	Extrel CMS model 150-QC
1.2 MHz	Extrel CMS model 150-QC
1.44 MHz	Pfeiffer Vacuum Model QMH 410-3
1.7 MHz	Extrel CMS model 150-QC
2.1 MHz	Extrel CMS model 150-QC
2.8 MHz	Extrel CMS model 150-QC

The center lens element of the einzel lens was maintained at -400 V.

For each quadrupole / RF frequency combination, the extraction lens voltage, Einzel lens 1 & 3 voltage, optimized for maximum sensitivity at 0.7 amu peak width at half height, and for RF-only operation.

Peak profiles were captured for each combination of RF frequency and rod diameter, with peak width at half heights of 0.18 amu, 0.35 amu, 0.7 amu, 2 amu, 5 amu, and 10 amu, using the 0.7 amu tune, and for RF-only, using the RF-only tune. Limitations in the range of operation of the 1.44 MHz RF supply did not allow for peak shapes at some of the wider peak widths to be measured, including RF-only spectra.

All intensity measurements were performed using the faraday aperture plate of the electron multiplier detector with the electron multiplier and dynode disabled, with 10^9 gain, 100 mV = 100 picoamps.

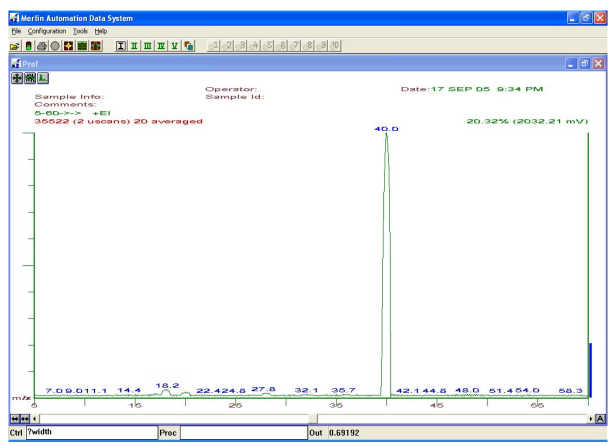

Figure 2. Typical mass spectrum showing peak shape and low relative level of background species (m/z 8, 20, 28, 32). (20 mm quadrupole, 1.2 MHz, scanning from 5 to 60 amu mass range)

III. RESULTS AND DISCUSSION

A large data set was gathered, with representative data shown in tables 3 and 4, illustrating unit mass resolution and RF-only results respectively.

Data were collected at a number of resolutions, with replicate data sets taken for most of the combinations of rod diameters and frequencies.

Data sets for other mass resolutions are presented in the appendix.

A simple analysis of the data in table 3 demonstrates the more dramatic dependence of intensity on rod diameter than on RF frequency.

Consider the lowest frequency data set (0.88 MHz). As rod diameter is increased from 6 mm to 20 mm, (a factor of 3.33 increase in rod diameter), the intensity is increased by a factor of 26.8, suggesting that transmission is approximately proportional to rod diameter cubed, for cases where the emissive area of the ion source is much bigger than the acceptance area of the quadrupole.

This relationship seems to be consistent with the smaller diameter quadrupoles operated at 1.44 MHz, specifically, one would predict that reducing the rod diameter from 6 mm to 4 mm would result in a sensitivity reduction of $(6/4)^3$, or 3.375-fold. The experimental result showed a reduction of 3.6, well within the experimental error for this single data point.

For a 6 mm quadrupole, an increase in RF frequency from 0.88 MHz to 2.8 MHz (a factor of 3.18 increase in RF frequency) results in an intensity increase by a factor of only 7.5, roughly proportional to frequency squared.

Other rod diameters and frequencies demonstrate a similar trend of stronger influence of rod diameter than frequency on sensitivity, although with less dramatic slopes. For a 9 mm quadrupole, the increase in sensitivity with increase in frequency was only a factor of 3.64 from 0.88 MHz to 2.8 MHz, suggesting an almost linear relationship between frequency and sensitivity for this data set.

For the 1.2 MHz RF supply, increasing rod diameter from 6 mm to 20 mm results in a 17-fold increase in intensity.

Clearly we are seeing a saturation effect, hypothesized to be related to the relatively limited emissivity of the ion source area relative to acceptance of the larger rod diameter quadrupoles.

Analysis of the data in table 4 helps illustrate this saturation effect. With the 20 mm quadrupole, the RF-only intensities are within a ten percent range of each other, with the scatter attributable to experimental error.

Table 3. Measured Peak Intensities (in millivolts) for various combinations of RF frequency and quadrupole rod diameter at 0.7 amu peak width, tuned for optimum sensitivity at 0.7 amu peak width.

Rod Diameter	RF Frequency (MHz) 0.88	1.2	1.44	1.7	2.1	2.8
4 mm			64			
6 mm	110	168	231	580	779	832
9 mm	558	991	1,280	1,809	1,944	2,031
12 mm	885	1,162	1,638	2,058	1,919	1,756
20 mm	2,951	2,857	3,117	2,828	2,616	2,335

Assuming that this represents all of the ions available for detection, the 20 mm quadrupole shows a remarkable 25 – 35% transmission for all of the RF frequencies.

The absolute ion currents at unit mass resolution are reasonably constant for the lower frequencies tested, but the relative transmission reduces at higher RF frequencies. These experiments were reproduced on a different day to verify this trend.

It is hypothesized that this phenomenon can be attributed to the effects of fringing fields at the entrance and exit of the quadrupole, as the higher frequency operation required much more negative entrance and exit lens voltages to achieve optimum sensitivity (-60 volt entrance, and –370 volt exit lens voltages for the 2.8 MHz 20 mm quadrupole, compared with a more typical range of +5 to –10 volts for the entrance lens, and 0 to –20 volts for the exit lens for most of the other data sets.)

For the 6 mm quadrupole, the RF-only data showed that the acceptance of the RF-only quadrupole is dependent upon RF frequency, but not as dramatic as for resolving operation as shown in Table 3.

Table 4. Measured Peak Intensities for various combinations of RF frequency and quadrupole rod diameter. (RF-only spectra, with RF-only tune)

Rod Diameter	RF Frequency (MHz) 0.88	1.2	1.7	2.1	2.8
6 mm	4,046	4,974	5,199	5,333	5,700
9 mm	6,339	6,953	7,165	7,540	7,558
12 mm	6,957	6,837	8,993	8,072	8,433
20 mm	8,764	8,981	9,727	9,045	8,815

IV. CONCLUSIONS AND FUTURE WORK

The overriding conclusion from this work is that absolute transmission of quadrupoles is much more dependent upon rod diameter than on RF frequency, although there is a strong correlation between sensitivity and both rod diameter and RF frequency.

For the typical case where the emissive area of the ion source is much larger than the acceptance of the quadrupole (i.e. in these studies, for the 880 kHz RF power supply), then **transmission appears to be proportional to rod diameter to the third power!**

Similarly, based on the 6 mm quadrupole data**, transmission appears to be proportional to RF frequency squared.**

If one were to extrapolate to smaller rod diameter quadrupoles, ion signal will be compromised severely, as the cross section of the ion source accepted by the quadrupole shrinks dramatically with reduction in rod diameter.

Future work in this project includes testing the performance of the quadrupoles with a much larger emissive area ion source. We have manufactured but not yet tested a molecular beam ionizer that is scaled to have just over three times the diameter for the ion volume (3/8 inch diameter ionizing region in standard, 1.25 inches in the new design), as well as three times wider diameter extraction lens (changing from 0.125 inches to 0.375 inches).

We are also in the process of manufacturing four inch long versions of the 6, 9, 12, and 20 mm quadrupoles, as well as four inch long quadrupoles with one and two millimeter rod diameters.

If our hypothesis that the acceptance of the quadrupole is saturated with a 0.375 inch diameter ion source with a 0.125 inch diameter extraction lens for all but the 6 mm quadrupole, then tripling the dimensions of the ionizer should serve to broaden the emissivity of the ion source to be larger than the acceptance of the quadrupole, and hence show more consistent shifts in sensitivity as rod diameter and frequency are increased.

Operating with one and two mm rod diameter quadrupoles would allow more accurate extrapolation of performance to smaller rod diameters.

V. ACKNOWLEDGEMENTS

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VI. APPENDIX

The following tables show representative measured intensities for various resolutions. Note that the system was tuned for optimum sensitivity for 0.7 amu peak width for all but the RF-only data.

There was a distinct difference in measured intensities between the RF-only tune and the resolved tunes. The 0.7 amu peak width tune was close to optimum for the other mass resolutions.

Table 3 is reproduced here as table 7 for completion.

There was not enough command resolution with a 16-bit DAC for data acquisition at the highest resolutions for the 4 mm and 6 mm quadrupole.

Table 5. Measured Peak Intensities (in millivolts) for various combinations of RF frequency and quadrupole rod diameter for 0.18 amu peak width.

Rod	RF Frequency (MHz)					
Diameter	**0.88**	**1.2**	**1.44**	**1.7**	**2.1**	**2.8**
6 mm				72	132	
9 mm	23	44	143	686	774	1,120
12 mm	54	209	267	623	852	1,094
20 mm	747	945	1,137	1,367	1,313	1,064

Table 6. Measured Peak Intensities (in millivolts) for various combinations of RF frequency and quadrupole rod diameter for 0.35 amu peak width.

Rod	RF Frequency (MHz)					
Diameter	**0.88**	**1.2**	**1.44**	**1.7**	**2.1**	**2.8**
4 mm			9			
6 mm		40	105	257	358	583
9 mm	278	374	636	1,183	1,277	1,541
12 mm	394	615	782	1,254	1,458	1,410
20 mm	1,384	1,905	2,364	2,124	1,976	1,607

Table 7. (same as table 3) Measured Peak Intensities (in millivolts) for various combinations of RF frequency and quadrupole rod diameter for 0.7 amu peak width.

Rod	RF Frequency (MHz)					
Diameter	**0.88**	**1.2**	**1.44**	**1.7**	**2.1**	**2.8**
4 mm			64			
6 mm	110	168	231	580	779	832
9 mm	558	991	1,280	1,809	1,944	2,031
12 mm	885	1,162	1,638	2,058	1,919	1,756
20 mm	2,951	2,857	3,117	2,828	2,616	2,335

Table 8. Measured Peak Intensities (in millivolts) for various combinations of RF frequency and quadrupole rod diameter for 2 amu peak width.

Rod	RF Frequency (MHz)					
Diameter	**0.88**	**1.2**	**1.44**	**1.7**	**2.1**	**2.8**
4 mm			355			
6 mm	442	693	1,263	1,571	1,679	1,501
9 mm	1,310	2,249	2,764	2,932	2,738	2,579
12 mm	1,611	1,838	2,761	2,481	2,115	2,227
20 mm	4,650	3,414	3,811	3,398	3,127	3,002

Table 9. Measured Peak Intensities (in millivolts) for various combinations of RF frequency and quadrupole rod diameter for 5 amu peak width

Rod	RF Frequency (MHz)					
Diameter	**0.88**	**1.2**	**1.44**	**1.7**	**2.1**	**2.8**
4 mm			635			
6 mm	1,222	1,619	2,187	2,759	2,445	2,030
9 mm	2,368	3,526		3,400	3,147	2,919
12 mm	2,535	2,054	2,830	2,647	2,314	2,542
20 mm	5,432	3,780		4,030	3,479	3,270

Table 10. Measured Peak Intensities (in millivolts) for various

combinations of RF frequency and quadrupole rod diameter for 10 amu peak width.

Rod Diameter	RF Frequency (MHz) 0.88	1.2	1.44	1.7	2.1	2.8
6 mm	2,040	2,456	2,900	3,372	2,993	2,578
9 mm	3,279	4,359		3,661	3,504	3,216
12 mm	3,208	2,408		2,897	2,666	2,901
20 mm	5,898	4,095		4,654	3,752	3,270

Table 11 (same as Table 4). Measured Peak Intensities for various combinations of RF frequency and quadrupole rod diameter. (RF-only spectra, with RF-only tune)

Rod Diameter	RF Frequency (MHz) 0.88	1.2	1.7	2.1	2.8
6 mm	4,046	4,974	5,199	5,333	5,700
9 mm	6,339	6,953	7,165	7,540	7,558
12 mm	6,957	6,837	8,993	8,072	8,433
20 mm	8,764	8,981	9,727	9,045	8,815