Home Built Mass Spectrometers

The Development of a Simple Quadrupole Gas Analyzer

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I. INTRODUCTION

About a year ago I thought it was time to use some of the vacuum equipment that I had been collecting for many years. The kind of project that appealed to me involved working with ion beams in some manner. I had already done some work with electron beams which are easy to produce but I had no feel for what to expect in the ion field. The books pertaining to ions weren't of much practical help in telling me what to expect in the way of the magnitude of the ion current that could be obtained or in providing any design details for building an ion source. So the first step was to build something and make some measurements. I'd either get some measurable results from which to take the next step or nothing would show up in which case I'd return to writing computer programs. A programmer friend of mine suggested that it would be much easier to just write a computer program to simulate the ion optics. My reply was that I could also simulate a dining program but that after I ran it I'd still be hungry! So I set out to build hardware.

II. STEP ONE - TIME-OF-FLIGHT

A simple Time-of-Flight mass spectrometer seemed like a good starting point. A beam of electrons from a tungsten filament (I had saved some tungsten wire) perpendicular to the axis of the vacuum enclosure would be directed into a cylindrical chamber where electrons would collide with residual gas molecules and ionize them. A repeller with a positive potential would push the resultant positive ions along the axis of the enclosure (a brass tube) toward a cylindrical electrode with a negative potential with respect to the ionization chamber. This is similar to a simplified Bayard-Alpert ionization gauge except that instead of collecting the ions on a wire, they are directed along the axis of the enclosure. An important provision in this project was to build most of the equipment using equipment and materials on hand or easily available at the local hardware store. The extraction cylinder was thus formed from a one inch diameter brass tube originally intended as a shower curtain rod. Success!

Measurable ion currents were collected on an electrode about eight to ten inches down stream from the exit orifice of the ionization chamber. An extraction potential of about 100-200 volts was sufficient. The detector was an ordinary 199.9 millivolt full scale DVM.

These inexpensive units can have input impedances of over 10^{12} ohms with bias currents of the order of 2 picoamps. A 1000 Megohm resistor across the voltmeter input provides a crude 199.9 picoamp full scale current meter. The ion currents generated using this equipment were in the nanoamp range! This was indeed encouraging. The next step was devising a way of discriminating the time of arrival of the various ions. Before doing this it was desirable to get an idea of the flight times of various likely ions. So the first thing to do was to work out the expected ion velocities. Here is where mathematical software came in handy. I used Mathcad, a product of Mathsoft, Inc. of Cambridge, MA. It went like this:

The velocity of an ion falling through a potential of E volts is:

$$v = 1.38\left(10^6\right) \times \left(\frac{E}{m}\right)^{0.5} \quad \text{cm/sec}$$

where m is the mass in AMU.

The graphs of Figure 1 on the next page are plots of velocity for several energies and masses ranging from 4 to 60 AMU. These graphs show that the velocities are going to be in the range of a half a million to over five million centimeters per second. If the flight tube is a half meter in length (I don't have a lot of room in my shop), then it will be necessary to handle flight times as short as $50/7 \times 10^{-7}$ seconds (~0.7 ms) for helium ions at 100 volts acceleration. In addition this time interval needs to be resolved to better than one divided by the mass number in order to be able to resolve one mass unit. At mass 50 the flight time is about two million centimeters per second or 2.5 μs with a resolution requirement of better than 0.05 μs. These things don't seem impossible with relatively simple equipment until the next step and trying to figure out how to make accurate time measurements on such tiny currents. At this point it becomes apparent that a very high gain, very fast,

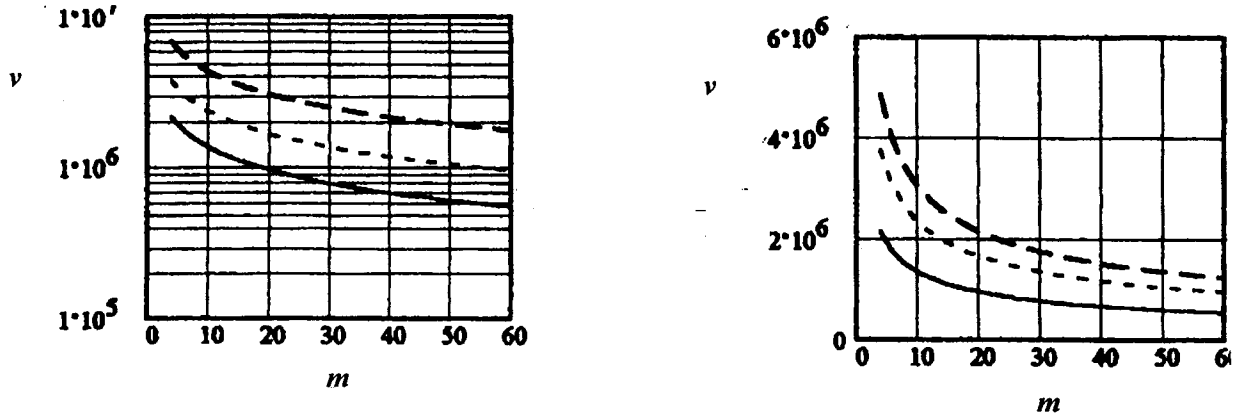

Figure 1 - Ion Velocities in cm/sec vs Mass in AMU. Left plot is log scale for velocity, right is linear scale. Dashed line is for 10 eV, dotted line is for 30 eV, solid line is for 100 eV.

current amplifier that has a low output impedance is needed so that fast IC gates can be used. Unfortunately that amplifier is the dynode assembly of an electron multiplier. I didn't have one available so it was time to review options.

III. STEP TWO - MAGNETIC SEPARATION

Maybe a magnetic mass separation approach would be fruitful. I'd saved some old electromagnetic focus coils from very early TV sets and knew that each one contains about 4500 turns of No. 29 gauge copper wire around a roughly two inch diameter core. It so happened that I had an iron bar 1-3/4 inches in diameter and enough other iron to build a complete electromagnet with a half inch air gap. This is just right to accommodate the small dimension of X-Band waveguide (which I had also saved). Assuming that most of the ampere-turns are consumed by the air gap, it looked as though it would be possible to develop a magnetic flux density of 2000 to 2500 gauss without overheating the coils. Now it was time to see whether flux densities of this magnitude could lead to a working mass spectrometer. Back to Mathcad.

The radius of curvature of the path of a singly charged ion accelerated by a potential E is given by:

$$r = 145(Em)^{0.5/B} \quad \text{cm}$$

where E is in volts, m is in AMU and B is the magnetic field in Gauss. Figure 2 is a graph showing a few reasonable parameter values.

The radius of the magnet pole pieces in centimeters is 1.75x2.54/2 = 2.22. It is obvious that the values of flux density easily achievable with the electromagnet are not capable of bending a beam of 100 eV ions through

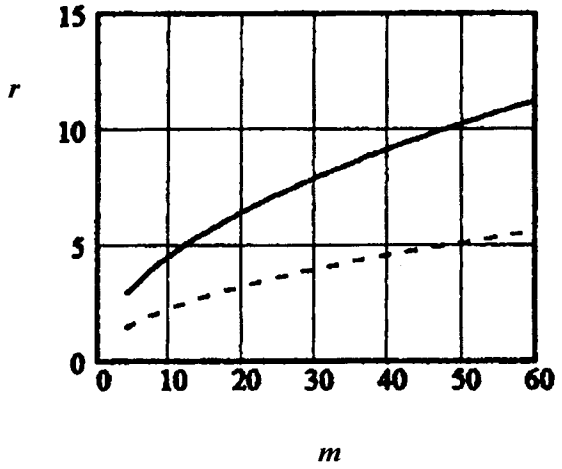

Figure 2 - Radius of Curvature in cm vs Mass in AMU at 100 eV. Solid line is for 1000 Gauss, dotted line is for 2000 Gauss.

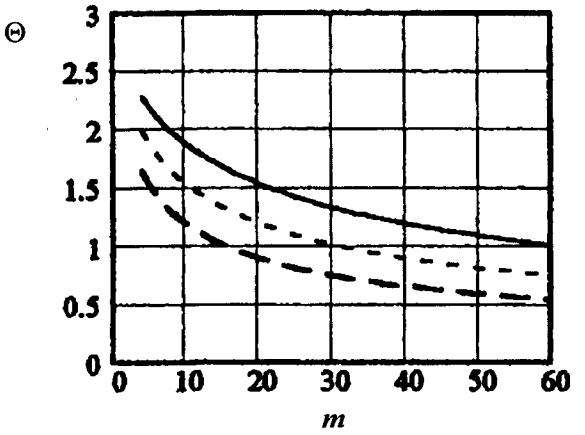

Figure 3 - Deflection Angle in Radians vs Mass in AMU at 2000 Gauss. Solid line is at 50 eV, dotted line is at 100 eV, dashed line is at 200 eV.

90° except for the very light ones. So it is necessary to check out smaller deflection angles. The deflection angle is given by:

$$\theta = 2\arctan\left[\frac{rB}{145(Em)^{0.5}}\right] \text{ radians}$$

This is depicted in Figure 3 for B equal to 2000 Gauss.

By restricting the ion energies to 50 volts max. it should be possible to use a deflection angle of 60° and still handle ions up to 60 AMU. The mass selection can be made by adjustment of B or E. It should be pointed out here that this arrangement involves geometrical considerations. The ions emerge from a physically defining aperture and are resolved at the detection end by a similar aperture. To get good resolution it is necessary to use small apertures - at least in the direction in which the magnetic field moves the beam. Tiny circular apertures are impractical because they severely restrict the available ion current. It is necessary to resort to narrow slits. A focusing means must also be provided.

The first design that led to some ion separation used narrow slits cut into disks of 0.010" brass shim stock. The part of the unit that was in the magnetic field was a piece of X-Band waveguide with a 60° bend, the center of which coincided with the center of the magnetic field. A crude Faraday cage was mounted behind the exit slit. Results were not spectacular but changing the magnetic field strength did run the detected ion current from some very low value to a peak and back down again to a low value. In fact, one run revealed two peaks.

The problem here was twofold. First I had no good way of measuring the flux density accurately in order to calculate what mass is being detected. Second, the hysteresis present in the magnet made repeating measurements difficult. The most important lesson here was the realization of how detrimental beam aberrations can be. Any defocusing of the beam affects the achievable mass resolution in a negative way.

Going back to the curves of Figure 3, what they indicate is that a change of one mass unit at mass=28 results in roughly three degrees of beam deflection. This isn't bad but the entrance slit had to be to .032 inches wide to get a measurable ion current. Beam aberrations make things difficult.

The plan was to use a simple three disk Einzel lens following the ion source slit to focus the beam on the Faraday cage slit. The image distance from the source slit was much shorter than the object distance to the detector resulting in a magnification of the beam width - definitely not good for resolution. Severe spherical aberration in the Einzel lens further deteriorated the mass resolution.

In spite of the foregoing, it was possible to demonstrate the control of an ion beam which was the initial objective of this effort. As is usual with home experimentation, the goals keep shifting in the direction of further refinement.

It appeared that any substantial improvement in performance would require a stronger ion beam and a more sensitive detector. A Burr-Brown 3522 op-amp helped with the latter but getting a stronger ion beam might be rather elusive. During the course of browsing the Internet in search of any hints for constructing an improved ion source, I chanced upon the home page of Professor Peter Williams in the Chemistry Department at Arizona State University. It was through his kind advice and guidance that I finally achieved my original goal. He suggested an excellent book for those inclined to build experimental equipment entitled "Building Scientific Apparatus" [1]. It proved to be extremely helpful.

IV. STEP THREE - ELECTROSTATIC SEPARATION: WIEN FILTER

One of the intriguingly simple mass filters referred to in this book is a Wien Filter. It is an inline configuration in which a set of electrostatic deflection plates produce an E-field perpendicular to the magnetic field - both of these being perpendicular to the axis of the ion beam. For a given beam energy (measured in electron volts) only a narrow range of masses can traverse the fields and exit through the output aperture. Dr. Williams warned me of the problems this deceptively simple approach would encounter but ventured that I'd probably try it to see for myself. He was absolutely right! It is very difficult to achieve the highly uniform fields required for this scheme to work. The results were poor but he had suggested that a quadrupole mass spectrometer (also referred to in Moore) was much more tolerant of beam characteristics. Even though I had briefly considered this approach at the beginning of the project, it looked too difficult and it didn't appear to be amenable to simple analysis like the other approaches. What I am about to describe is the effort that resulted in the present design.

V. STEP FOUR - ELECTROSTATIC SEPARATION: QUADRUPOLE FILTER

A quadrupole mass spectrometer uses a saddle-field lens (one whose electric field in three dimensions looks like a saddle) that is created with simultaneously supplied ac and dc potentials. In the absence of ac the only stable position for a charged particle in the lens is directly on its center axis. The slightest movement from the center will subject it to an accelerating or decelerating force. If the particle is a positive ion and moves toward a positive pole (one of four symmetrically spaced rods with opposite rods connected electrically), it will be pushed back toward the axis.

If the positively charged particle moves toward a negative rod, it will experience an attraction and keep going until it hits the rod. Because the ion has mass, it cannot accelerate instantaneously and therefore it must take a finite amount of time to travel a given distance toward the rod. If during the period that the ion is moving to a rod, if that rod reverses its polarity, the ion will reverse its course and move back toward the center.

The time to travel to the rod is, of course, dependent upon the mass of the ion, its charge, and the intensity of the electrostatic field. It turns out that there is a combination of dc and ac potentials along with the ac frequency that will capture (resonate) an ion of a given mass and constrain it to remain within the quadrupole assembly. All other masses, given sufficient time, will strike one of the rods.

The axial motion of the ion is what determines how long the ion will remain in the assembly. It has to remain long enough so that an ion one resolvable unit higher or lower will not make it through the quadrupole.

OK, where does one start? Moore and a 1963 paper by Woodward and Crawford [2] provided the foundation.

The equations for the voltages applied to the two pairs of rods are:

$$V_1 = V_{dc} + V_{rf}\cos 2\pi ft \quad \text{and} \quad V_2 = -V_{dc} - V_{rf}\cos 2\pi t$$

The optimum ratio of *Vdc/Vrf* is given as approximately 0.17. The selected mass for singly charged ions is given as:

$$m = 0.14\left[\frac{V_{rf}}{r^2 f^2}\right] \quad \text{AMU}$$

where r is in cm and f is in MHz.

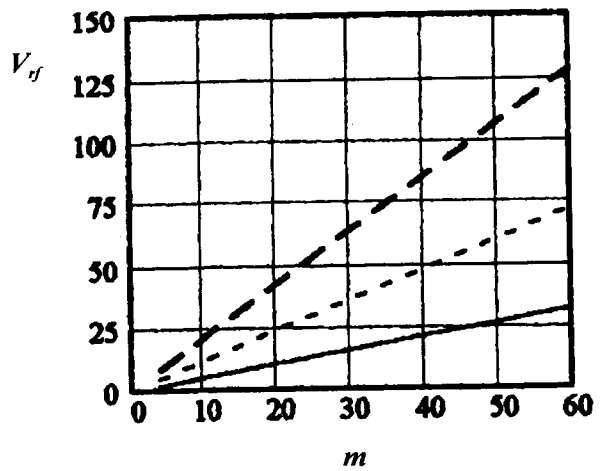

Figure 4 - Peak RF Voltage for Quarter-Inch Rods. Inscribed radius is 0.273 cm. Dashed line is for 1.0 MHz, dotted line is for 1.5 MHz, Solid line is for 2.0 MHz.

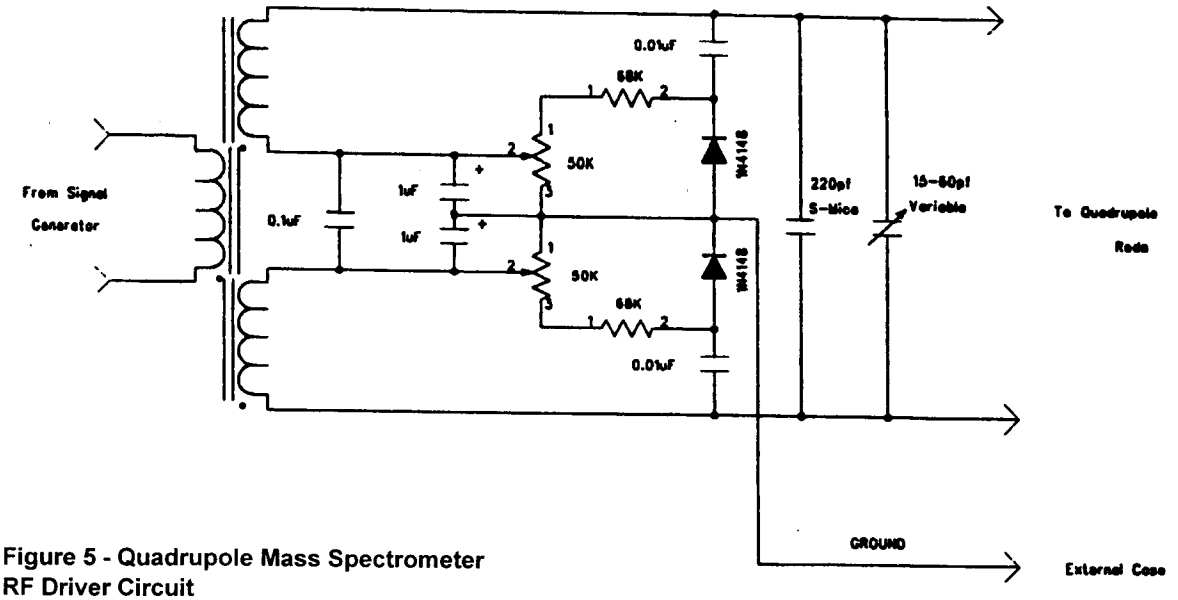

Figure 5 - Quadrupole Mass Spectrometer RF Driver Circuit

This can be rewritten to show how V_{rf} depends upon the other parameters:

$$V = 7.14mr^2f^2$$

It turns out that circularly cylindrical rods arranged so that the inscribed diameter of the assembly is 0.86 times the diameter of the rods provide a good approximation to the desired saddle-field. Quarter-inch diameter brass rods seem like a good starting point. The inscribed radius r will be 0.273 cm. As usual, Mathcad can help to make further dimension selections. Figure 4 shows plots for peak rf voltage with quarter-inch rods.

Preliminary tests using a waveform generator capable of providing 10 volts p-p into a 50 ohm load showed that a bifilar coil wound on a toroidal ferrite core could produce 1.5 MHz sine waves with peak values of 80 to 90 volts when using a few turns for the primary. Thus a 1.5 Mhz driver could allow mass selection up to 60 AMU. At these levels it appeared possible to build a relatively simple circuit to drive the rods. Diodes would be used to obtain the dc voltages and these would be summed with the rf.

A schematic for the resulting design is shown in Figure 5. The 1N4148 diodes are capable of rectifying peak RF voltages up to 80 volts to produce the DC needed. The transformer consists of a two turn primary of #26 enameled wire wound over a bifilar secondary of 70 turns of #26 wire on a Micrometals T 80-6 core. The tuning capacitors shown in the schematic tune the unit to 2Mhz. (The tests being described in this article were done at 1.5 MHz.)

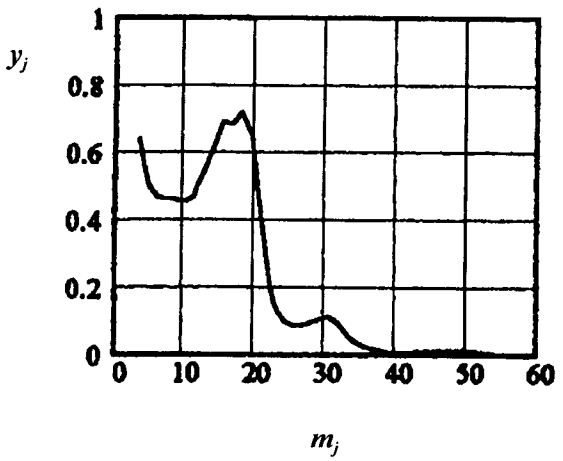

Figure 6 - Spectrum Showing Ion Current vs Mass. 1/4" diameter rods, 2" long.

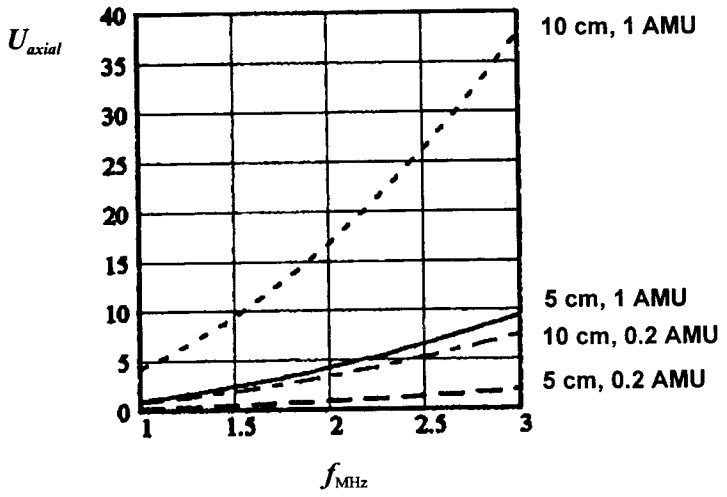

Figure 7 - Allowable Axial Velocity (Expressed as Voltage) vs Frequency for Various Rod Lengths and Resolutions.

The 50K Trimpots adjust the dc to peak rf ratio. Tuning the unit to select a given mass is done simply by adjusting the drive level from the waveform generator. The Q of the resonant transformer is quite high (over 100) so that a square wave can be used as the drive if desired. At this point the results of the first set of tests will be presented.

VI. FIRST RUN TEST RESULTS

The first run results for 1/4" diameter rods, 2" long are shown in the Mathcad plot of Figure 6. The variable y_j is the relative ion current detected and m_j is the DC voltage converted to AMU. Note the relatively poor mass resolution and the change in sensitivity that occurs as the mass increases. This result led to further analysis to see how to improve the resolution. (Originally a demonstration of the presence of two peaks would have been declared a victory and the project put to bed in favor of some other endeavor but goals change easily).

VII. OPTIMIZING THE QUADRUPOLE SENSOR

The original estimation of mass resolution as a function of assembly length and ion axial velocity was based on a heuristic approach that argued that the number of rf cycles that the ion should remain in the quadrupole should be equal to or greater than the mass number. The 2" long 1/4" diameter rods selected for the first design looked reasonable until a decimal point error was discovered! No wonder the first results were as they were. (Back to Mathcad for some more analysis.)

Woodward and Crawford [2] cite design equations given by W. Paul who devised the approach. The maximum axial velocity (in volts) that an ion can have so that it will remain in the quadrupole assembly long enough to be selected is:

$$U \sim 4.2\left(10^{-2}\right) f^2 L^2 \Delta m$$

where U is the axial voltage, f is the oscillator frequency in MHz, L is the rod length in cm and Δm is the mass resolution in AMU. (Note, U is frequently used for voltage, especially in the German literature.)

Getting sufficient ion current to work with has been a problem using the existing equipment and low values of U_{axial} don't help the situation. A set of curves showing the allowable maximum for U_{axial} as a function of several selectable parameters should be useful in improving the design. Figure 7 is the Mathcad plot showing this.

It became obvious that the quadrupole assembly must be longer, at least 10 cm, and that a resolution of 0.2 AMU wasn't going to be easy. Operating at a higher frequency would be beneficial but the effect on the required peak rf voltage would have to be examined. Back to Mathcad. Figure 8 shows the peak rf voltage required for mass 60 for rod diameters of 1/8", 5/32" and 1/4".

OK, 1/8" rods 4" long (~10 cm) operating at 2 MHz looks like a good possibility. It might be possible to go to 3 MHz but this is about the limit for the simple driver that is already being used. Multiple mass resonances were obtained with this design but the collection of data point by point proved to be very tedious. A much easier method for detecting the presence of various ions was to use an analog panel meter at the output of the ion current amplifier. It was then easy to quickly find peak readings as the rf drive was changed - just like the old S-meters used for tuning Ham radios.

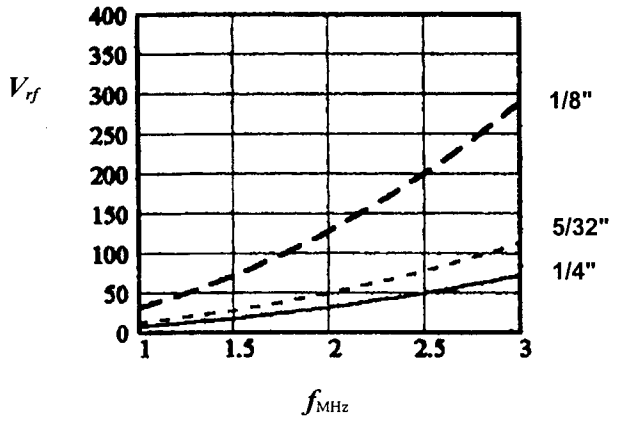

Figure 8 - Peak RF Voltage vs Frequency Required for Mass 60 with Various Diameter Rods at 0.2 AMU Resolution.

VIII. FABRICATION

Fabrication was generally driven by what was on hand. Screws were 2-56, 4-40 or 6-32. The outer case was a brass tube, 1-1/2" outside diameter of the type sold for railings. I used Bradford tubing from Home Depot. Brass brazing rod of various diameters worked for bringing out connections to the electrodes of the ion source. The rods were drilled and tapped for 2-56 screws to allow for the attachment of wires. These were terminated with a seven pin connector that communicated with the outside world. Almost all of the pieces were designed with a view to being machined on a lathe. Insulating elements were mostly epoxy-glass printed circuit board material with the copper removed. This was probably the weakest point in the system because of outgassing from the laminate material. Copper was used is places where it was felt that temperatures might be too high to use aluminum or where soldering was required to join two pieces. The largest collet available for my lathe was 5/8" which worked out well for handling 1/2" copper water pipe.

The epoxy glass disks were turned to a diameter slightly smaller than the inside diameter of the outer case so that the assembly would slide easily into the tube. The end caps were either brass or aluminum. In the case of the exit end of the device, a disk of 1/4" thick aluminum was used. The vacuum seal to the case was an O-ring that fit into a groove in a brass ring that was soldered to the outer tube. Six 6-32 cap screws fastened the disk to the outer case. Feedthroughs were Selectro FT-SM Press-Fit Teflon terminals. Three of these were used: two for connecting the quadrupole rods to the rf driver circuit and one for bringing out the center element of the Faraday cage. These terminals were not completely vacuum tight and had to be covered with epoxy or Glyptal to make a good seal.

Given the outgassing from the organics, the limited speed of my vacuum system, and a few residual leaks, no effort was made to provide for introducing gases into the system. Water was always present but none of the test runs lasted long enough to remove most of it.

A sketch of the main elements of the ion source is shown in Figure 9. The biggest problem is the filament. A 0.005" diameter tungsten wire takes over two amps to reach a milliamp or so of electron emission at a temperature of about 2500° K. The brass posts upon which it is mounted using 2-56 steel screws get very hot. These were originally supported by an epoxy-glass disk but the disk tended to char even though it in turn was fastened to a thick copper slug. A disk of mica sandwiched between the epoxy-glass disk and the copper slug which is part of the anode structure helped the situation. The only insulation the filament posts contact is the mica. The use of finer tungsten wire (e.g. 0.002" diameter) should probably be investigated.

A repeller electrode is placed behind the filament in the current instrument in an effort to direct the electrons into the anode chamber. Its effectiveness needs further investigation. A photo of the quadupole mass spectrometer is shown in Figure 10.

IX. SOME RESULTS

The approximate electrode potentials found to provide measurable ion currents are shown in Figure 11. Further work needs to be done to refine these potentials but they were successful in providing data that could be analyzed to point the way to improved performance.

Two sets of spectrum data are shown in Figure 12. Again, these were taken on a point by point basis and the resulting data files were plotted using Mathcad. Taking point by point data proved to be very tedious and difficult to take fast enough because of drifts in the filament emission and in the resonant frequency of the rf

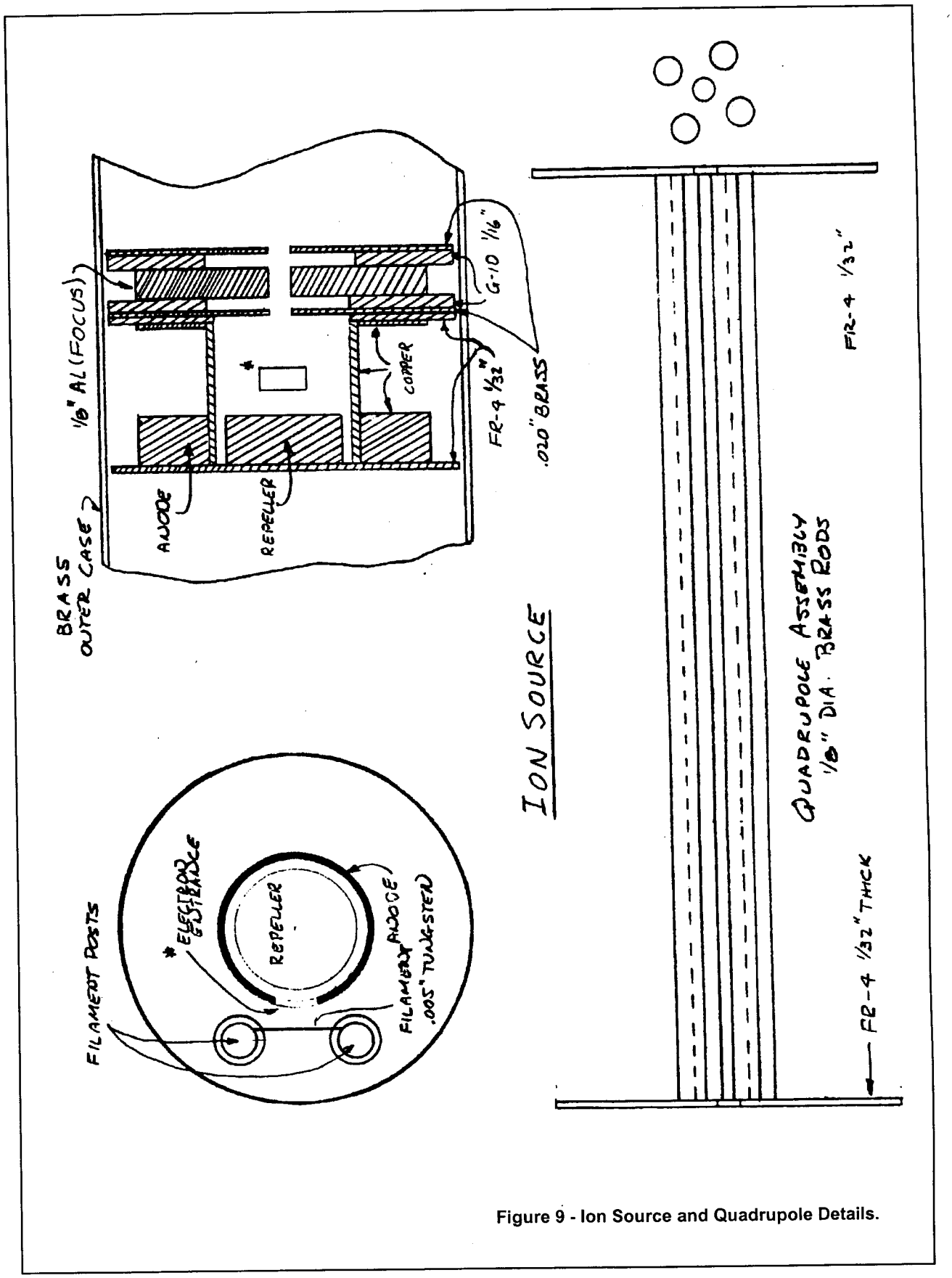

Figure 9 - Ion Source and Quadrupole Details.

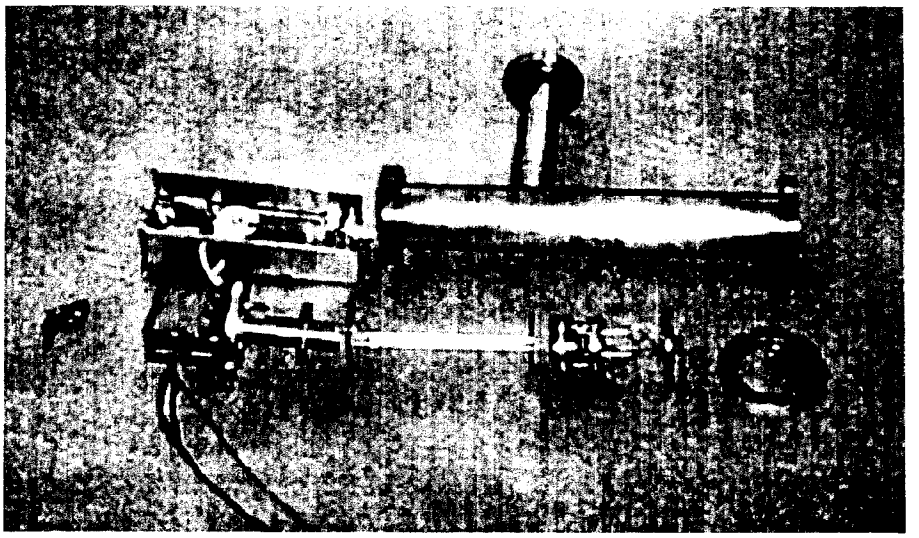

Figure 10 - Disassembled Quadrupole Mass Spectrometer

driver circuit due to temperature changes during operation. Neither of these problems is particularly difficult to solve but I needed some results to see if it was even worth considering further design changes. Note that with the ion repeller set at +48 volts with respect to the grounded exit aperture the axial velocity of the ions is too high to expect good mass resolution. But it was a start.

The two plots of Figure 12 were obtained for different ratios of V_{dc}/V_{rf}. The literature says that the optimum ratio is 0.16784 and that mass resolution degrades as the ratio is reduced. The data seem to bear this out. The ordinates in both cases are in picoamps. Measured ion current below the equivalent of mass 15 become very large and erratic - I can't explain this except to guess that the resolution is so poor below this number that the roughly 50 eV ions are not filtered by

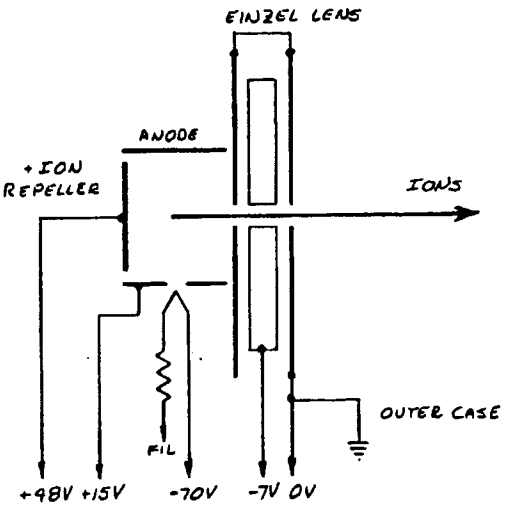

Figure 11 - Ion Source Schematic with Electrode Potentials.

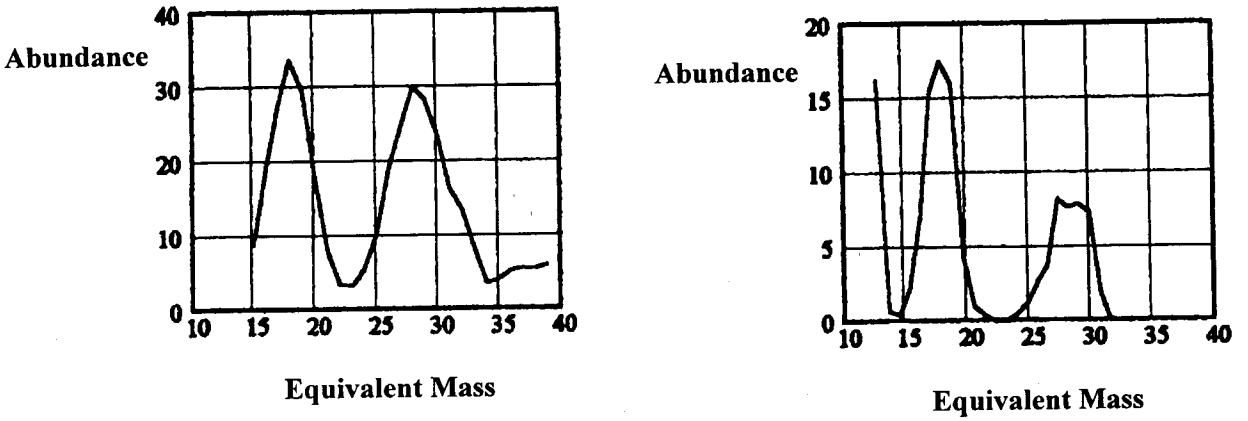

Figure 12 - Mass Scans. Left plot is for V_{dc}/V_{rf}=0.137, right is for V_{dc}/V_{rf}=0.16.

the quadrupole filter. The voltages are so low in this region that they have little influence in affecting the paths of the energetic ions. At zero volts on the quadrupole, adjustments of the ion source potentials can be made that allow electrons to get to the Faraday cage.

X. CONCLUDING COMMENTS

Where does all this lead? Well, I did get to play with ions and I was able to move them around in at least a qualitatively predictable fashion. I was able to measure picoamp currents and I did learn something about designing a couple of mass spectrometers and about why some types are easier to build than others. And finally, I saw something work - not just a simulation.

What's next? Maybe I'll build a higher voltage driver with more precise control of the potentials and their ratios. I'll probably design and build a filament emission regulator to remove that source of drift and I'll likely design a data logging interface so that my computer can do the scanning and data plotting without my help.

Before doing any of this, however, I need to do a lot more experimenting with ion sources. In this regard, I want to recommend a software program that I downloaded from the Internet called "EFIELD" [3]. It was written by Dr. Alex Tolmachev, a researcher associated with the Russian Academy of Sciences. This program let me check out the properties of the ion source configuration I used. The program lets you plot ion trajectories for various combinations of electrode potentials and even plots the electric field contours and field lines for you. It proved to me how difficult it is to get the field uniformity needed by the Wien Filter.

Having some insight into how electrode potentials affect ion trajectories does a lot for ones willingness to start up the vacuum system for checking a modified design. Once the pump down starts there is little one can do but change potentials. The guidance EFIELD provided was invaluable.

REFERENCES

1. John H. Moore, Christopher C. Davis, and Michael A. Coplan, *Building Scientific Apparatus* (Addison-Wesley, 1983).
2. C.E. Woodward and C.K. Crawford, *Design of a Quadrupole Mass Spectrometer*, MIT, 1963.
3. Alex Tolmachev, *EFIELD*. This DOS-based freeware program may be downloaded from the Web site of the Charged Particle Optics Group, Delft, the Netherlands at http://wwwdo.tn.tudelft.nl/bbs/software/index.htm. You may not be able to download this with Netscape 3.0 or Microsoft Explorer. However, the Mosaic browser and Netscape 2.0 worked.

ABOUT THE AUTHOR

Carl Helber graduated from Ohio State University with a BS in Engineering Physics. He spent the first half of his professional career involved in radar research and development and the latter half in industrial control design and fabrication for electronic test and process control equipment as used in the semiconductor industry. Today his interests include working on physics related experiments, especially those involving high vacuum, electronic design (including electronic organs), and computer programming.