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Development of a Portable Mass Spectrometer for Operation at 1 Torr

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Development of a Portable Mass Spectrometer for Operation at 1 Torr

by

Feng Jin

**Dissertation submitted
to the Eberly College of Arts and Sciences
at West Virginia University**

in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy in
Chemistry**

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2014

Keywords: Portable Mass Spectrometer, Tuning Circuit, Loeb-Eiber Mass Filter

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ABSTRACT

Development of a Portable Mass Spectrometer for Operation at 1 Torr

Feng Jin

Portable mass spectrometers have obtained increased interest because they show great potential in different fields such as the industrial process analysis, forensic science, environmental monitoring, space exploration and homeland security. Most portable mass spectrometers are based on bench-top instruments, but on a smaller scale. Examples include small quadrupoles, magnetic sectors and ion traps. In contrast, the mass filter developed in this work has no bench-top-scale equivalent. It is inherently miniature and was first demonstrated back in 1963.

The Loeb-Eiber mass filter developed in this work is suitable for development for portable mass spectrometers, although the device has so far only been demonstrated in breadboard fashion in bench-top vacuum chambers. The second generation Loeb-Eiber mass analyzer developed herein uses an array of short wires attached on a non-conductive base instead of two long wires spooled on the base, which greatly improves ion transmission to 25% from 6.25% of first generation analyzer. Also, the capacitance of the second generation mass filter is reduced to 70 pF from 5000 pF of the first generation. The third generation Loeb-Eiber mass analyzer is fabricated based on silicon-on-insulator (SOI) using microelectromechanical system (MEMS). The Manhattan electrode geometries are therefore square in cross-section compared to the round cross-section of the originally tested electrodes. Square cross-section electrodes have several benefits over round cross-section electrodes, such as the ability to filter ions at lower

frequencies, lower amplitudes, or higher pressure. This dissertation describes the construction and testing of a variety of ion sources and detectors with different prototype Loeb-Eiber mass filters. The dissertation also describes ion simulation to understand different modes of operation of the filter, rf-electronic design, construction and testing, and programming to enable digital control of all the electronic components and data acquisition. Different rf tuning circuits are also constructed to match the different mass filters. Glow discharge and electron ionization sources were also built and characterized.

DEDICATION

*To my mother for giving her love and providing me with everything and expecting
nothing but happiness.*

*To my beloved wife, without your love and support none of this would have been
possible.*

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LIST OF ABBREVIATIONS

EPA	Environmental protection agency
GC/MS	Gas chromatography/ mass spectrometry
TOF	Time of flight
rf	Radio frequency
ITMS	Ion trap mass spectrometry
MEMS	Microelectromechanical system
LTCC	Low-temperature cofired ceramics
SLA	Stereolithography apparatus
FWHM	Full width at half maximum
CCD	Charge-coupled device
KE	Kinetic energy
MALDI	Matrix-assisted laser desorption/ionization
SS	Stainless steel
AFSA	Acceleration/focusing/steering assembly
MMS	Miniaturized mass spectrometer
QMS	Quadrupole mass spectrometer
dc	Direct current
QIT	Quadrupole ion trap

CIT	Cylindrical ion trap
RIT	Rectilinear ion trap
GDEI	Glow discharge electron ionization
ESI	Electrospray ionization
APCI	Ambient pressure chemical ionization
DESI	Desorption electrospray ionization
CID	Collision induced dissociation
AC	Alternating current
VHF	Very high frequency
AFG	Arbitrary function generator
MF	Median frequency
HF	High frequency
EMF	Electromagnetic field
CAD	Computer aided design
VF	Velocity factor
SWR	Standing wave ratio
AWG	American wire gauge
SOI	Silicon-on-insulator
DRIE	Deep reactive ion etching

FFT	Fast fourier transform
PCB	Printed circuit board

CHAPTER 1: INTRODUCTION

1.1 Necessity of Development of Portable Mass Spectrometers

Mass spectrometers have become an indispensable tool in chemical analysis laboratories because of their high selectivity, accuracy and sensitivity. For example, some of the largest official organizations like ASTM (American Society for Testing and Materials) and the EPA (Environmental Protection Agency) lists GC/MS (gas chromatography/mass spectrometry) in many official methods. These methods are typically off-line chemical analyses using traditional bench top instruments. Bench-top instruments provide the highest resolution, sensitivity, mass range and robustness available to meet the needs of the analyses at the most affordable costs. Less important considerations for bench-top mass spectrometers are the size and power consumption, which can be in excess of 150 lbs and 50 W which limits the usage of mass spectrometers in field applications. Because bench-top instruments cannot leave the laboratory, samples must be collected, packaged, shipped and stored prior to analysis. During these steps, samples can undergo significant changes, degradation, evaporation, contamination and risk being lost or mishandled during time consuming transportation. These factors increase the burden and expense in method validation and analysis. Thus there is a demand to develop portable mass spectrometers to achieve real time detection with adequate performance for *in situ* analysis such as environmental analysis, space exploration, process control, and homeland security.

Janasek and coworkers introduced a scaling law developed for predicting the characteristics of miniaturized chemical analysis instruments.¹ This law is proved to be very accurate in predicting mechanical properties, but not accurate about electromagnetic and thermal behavior. If every side of an instrument shrinks by one half, the whole volume and mass of the instrument would reduce by a factor of one eighth. Scale reduction can therefore greatly reduce the weight and cost. When the size of a mass spectrometer decreases, ions will have a shorter distance to travel and thus can work at higher pressure, reduce the requirement for pumps.^{2, 3} Different mass analyzers benefit from size reduction differently. Ion trap mass analyzers benefit the most because they can have better resolution and sensitivity at relatively high pressure and buffer gas is required to cool ions or dampen ion trajectories. But for most mass analyzers, there is little benefit to miniaturization. High vacuum is still required to obtain unimpeded trajectory because the performance such as resolution and sensitivity depend on the vacuum. Moreover, miniaturization also facilitates use of relatively lower voltages in order to maintain the same electric field strength. This can reduce the size of tuning circuits, especially for dynamic mass spectrometers. Figure 1-1 shows the mass analyzer and rf (radio frequency) coil for a miniature ion trap and a commercial bench top ion trap mass spectrometer.⁴ The rf circuit of the Mini 11 developed by Cooks, Ouyang and coworkers allows scanning m/z up to 800. The full size quadrupole ion trap (ITMS) only has an upper m/z limit 650. The rf coil for miniature ion trap uses 15 W whereas the regular coil uses approximately 250 W.

Figure 1-1 Mass analyzer and rf coil comparison between a miniature ion trap (Mini 11) and the first commercial ion trap mass spectrometer (ITMS). Image reproduced from Reference 4 with permission.

Machining errors become a challenge for miniture mass spectrometer especially when the size becomes less than 1 mm. Traditional machining methods are not possible at these dimension, and methods such as microelectromachining system (MEMS) can instead be used to

fabricate many different mass analyzers including TOF mass analyzers,⁵ quadrupole mass analyzers,⁶ ion trap mass analyzers.^{7, 8} Other techniques including LTCC (low-temperature cofired ceramics),⁹ SLA (stereolithography apparatus).^{10, 11} and laser machining¹² can also be used to machine portable mass analyzers with complicated configurations.

1.2 Miniaturization of Mass Analyzers

1.2.1 Sector Analyzer (*Electric, Magnetic and Crossed Field*)

Sector analyzers are well known for their high resolution and mass accuracy. Sector instruments typically consist of a combination of electric (E) and magnetic (B) sectors (EB or BE), or multiple combinations BEB. Lab scale sector analyzers normally use heavy and large electro-magnetic sectors. But miniature magnetic sectors can use small permanent magnets instead, therefore they can consume less power compared to quadrupole and ion trap mass analyzers and are more robust.

The principle of sector mass analyzers is described below. Ions are resolved in a magnetic field according to the force equilibrium equation, as shown in Eq. (1) where m is mass of an ion, v is the velocity of the ion, z is charge of the ion, B is magnetic field strength, r_B is the radius of the ion's path.

$$\frac{mv}{z} = Br_B \quad (1)$$

From the first glance, this equation is a momentum to charge analyzer because of the mv term in the numerator, however, if the ions are accelerated by the same potential V into the analyzer, it will become a mass to charge analyzer considering kinetic energy equation, as shown in Eq. (2).

$$\frac{m}{z} = \frac{B^2 r_B^2}{2V} \quad (2)$$

When ions are analyzed in an electric sector, the force equilibrium equation is Eq. (3). In this equation, E is electric field strength and r_E is the radius of ions' path. Electric sectors therefore act as velocity filters.

$$\frac{mv^2}{z} = Er_E \quad (3)$$

Electric and magnetic sectors are commonly combined to achieve momentum filtering, which has the combined effect of mass to charge filtering. Two geometries are usually used to construct double focusing mass spectrometers, Nier-Johnson and Mattauch-Herzog. The Nier-Johnson geometry has two focus points, one is between the two sectors, and the other one is at the exit of magnetic sector. Either electric fields or magnetic fields need to be scanned to obtain mass spectrum. The Mattauch-Herzog geometry uses a focal plane to detect ions without scanning magnetic field. Thus, it can obtain mass spectrum simultaneously with high sensitivity.

Here are a few miniature sector analyzer reports that use Nier-Johnson geometry.¹³⁻¹⁵ An electric sector was followed by a magnetic sector which was maintained at pressure 10^{-6} Torr supplied by a sputter ion pump.¹⁵ Two electron multiplier detectors were used to acquire signal for high mass and medium mass channels. The instrument was demonstrated with resolution 150 at 5%-10% of peak height, mass range of 2-250 u, and sensitivity of 1 ppm. This mass spectrometer weighed 20 kg without the computer and consumed 30 W. Later, this instrument was used to determine heavy metals with concentration from 1 mg/l to 10 μ g/l in sea water¹⁴ and on-line monitor gas and volatile compounds at the ppb level.¹³

Another novel miniature double focusing sector mass analyzer was proposed by Diaz.¹⁶ It consisted of a 90-degree cylindrical crossed electric and magnetic sector with a radius of 2 cm. This superimposed structure can effectively remove the ions' angular and chromatic dispersion under certain conditions. Laboratory air was analyzed and nitrogen peak (m/z 28) was demonstrated with the highest mass resolving power 106 at full width half maximum (FWHM). The mass range was up to 103 u and detection limit was 10 ppm. The size of mass spectrometer was 7.5 cm $\times$ 6 cm $\times$ 3.5 cm.

Several miniature mass spectrometers with Mattauch-Herzog geometry has been designed to detect the effluent from microbore capillary columns.¹⁷⁻²⁰ These all share similar sector configuration, as shown in Figure 1-2. New magnet material was used to fabricate magnetic sector. Three miniature mass spectrometers with different focal planes of 12.7, 5.1 and

2.54 cm have been characterized with different mass range, 25-500, 40-240 and 2-250 Th (1 Th= 1 Da/Charge), respectively. The smallest analyzer of the three weighed 395 g with size of 10 cm $\times$ 5 cm $\times$ 5 cm. A modified 1000-pixel modified CCD (charge-coupled device) detector array was invented to measure ions up to m/z 250 with a unit mass resolution.²⁰ The sensitivity could reach to 2 μ A/Torr.

Figure 1-2 Schematic of double focusing mass spectrometer with Mattauch-Herzog geometry, reproduced from reference 17 with permission.

Besides double focusing mass spectrometers, a miniaturized single magnetic sector mass spectrometer was also reported to analyze the thermal evolved gas from thermal analyzer used in Phoenix mars mission, as shown in Figure 1-3.²¹ It consists of a permanent magnet with field strength 0.65 T and weight 500 g. The volume of the instrument was 24 $\times$ 23 $\times$ 18 cm and the weight was only 5.7 kg. The operating power was 13 W. Four ion trajectories with different radii were selected to cover the mass ranges 0.7-4, 7-35, 14-70 and 28-140 Da. The highest resolution was 140 obtained at high mass channel.

Figure 1-3 Schematic of a magnetic field mass analyzer for operation on the Martian Phoenix lander. Image reproduced from Reference 21 with permission.

In summary, the sector can be made very small especially for instruments using a permanent magnet. The consumed power is also smaller than mass spectrometers using rf power supplies and pulsed power supplies. High vacuum, lower than 10^{-6} Torr, is needed to maintain normal operation due to the requirement of collision-free ion transport. The mass resolution degrades dramatically with size reduction of magnetic sector.⁴ Adequate characteristics can be obtained depending on application.

1.2.2 Portable Time of Flight Mass Spectrometer Analyzers

A time of flight (TOF) mass spectrometer is another common mass spectrometer in chemical analysis labs. TOF has many advantages such as simple design, high resolving power, high sensitivity, non-scanning operation, large mass range and very high mass accuracy. All these benefits make miniaturized TOF one of promising portable mass spectrometers, even if the performance may degrade to some extent when the size becomes smaller.

The simplest TOF mass analyzer contains an extraction and acceleration region, a field free region and a detector. Ions at different m/z can be identified according to their respective flight time. For linear TOF analyzers, ions' motion follows Eq. (4) where V is accelerating voltage; t is flight time; d is the distance of ions' flight. The same voltage V accelerates all the ions and ions' mass to charge ratio is proportional to the square of its flight time.

$$m/z = \frac{2Vt^2}{d^2} \quad (4)$$

The ions may be not generated from exactly the same position in the extraction region with uniform kinetic energy (KE). Thus, the initial position spread and KE dispersion have a significant influence on the mass resolution of TOF analyzers. Time lag focusing technique is often used to compensate for position effects on resolution.²² The ion mirror or reflectron field is usually used to achieve energy focusing to improve resolution.²²

Cotter's group at the Johns Hopkins University have made many contribution towards the miniaturization of TOF analyzers.²³⁻²⁶ An end cap reflectron time of flight mass spectrometer was developed by this group, which consists of a sampling probe, laser ion source, endcap reflectron electrode and a channel plate detector, as shown in Figure 1-4.²⁴ The endcap assembly has a threaded rod that can tune the endcap electrode to achieve different focusing distances. The whole analyzer is approximately 5.08 cm in length. Samples were loaded on the probe and then ionized by laser beam. Ions entered a quadratic reflectron field and were reflected to a channel plate detector. Kinetic energy focusing was obtained in the reflectron. Bradykinin was tested in this mass spectrometer with the resulting mass spectrum shown in Figure 1-5. A peak at m/z 1061 shows resolving power of 210 using an accelerating voltage of 3.5 kV. Later, a drift region was added between detector and endcap electrode that increased the total length of mass analyzer to 6.35 cm.²⁷ Thus, time-delayed pulsed extraction can be utilized to optimize focusing. This modification improved the resolving power of the same peak to 330 with accelerating voltage 2.9 kV. The mass range was 3 kDa. At the same time, another TOF mass analyzer with a longer endcap reflectron was also built by the same group. Its mass range was comparable to commercial MALDI-TOF (matrix-assisted laser desorption/ionization time of flight) instruments.²⁵ In order to improve sensitivity, Cotter's group modified the position of end-cap electrode and detector to improve detection efficiencies.²⁶ Substance P was tested with a sensitivity of 3 fmol.

Figure 1-4 Schematic to show end cap reflectron time of flight analyzer. Schematic reproduced from Reference 22.

Figure 1-5 Mass spectrum of bradykinin obtained in the endcap reflectron TOF, reproduced from reference 24 with permission

A compact time-of-flight mass spectrometer with 8 cm field free region and 4 cm dual stage reflectron has also been developed.²⁸ An electrodynamic ion funnel was used to guide and focus ions to achieve maximum transmission. An ion acceleration/focusing/steering assembly (AFSA) was used to accelerate, collimate and deflect ions to achieve optimal spectral resolution. A schematic of this instrument is shown in Figure 1-6. Two turbo pumps and a dry scroll pump

were used to obtain a differential vacuum at approximately 1×10^{-2} Torr and 1×10^{-5} Torr in the ion mobility and TOF respectively. Both an in-vacuum ionization source and an atmospheric ionization source can be coupled to this miniature TOF. A 45 ns injection pulse provided optimal instrument resolving power. The preliminary results showed that isotopes of Xe could be resolved with a resolving power of 125. This mass spectrometer weighed 75 lb and measured $20 \times 20 \times 10$ inches.

Figure 1-6 A cross section view of a compact TOF system. Schematic reproduced with permission from Reference 26.

Another integrated TOF micro mass spectrometer has been designed using MEMS technology.²⁹ The cross section of this miniaturized mass spectrometer (MMS) analyzer was 5

mm×10mm. For this size scale, pressures ranged from 5 to 100 Pa is enough, and then a one-stage pumping was used in their MMS. In addition, lower voltage is needed to maintain the similar field strength with bench top TOF mass spectrometers. The highest voltage in this MMS was extraction electrode potential, only 95 V. The whole MMS was comprised of six major parts, the electron source, the ionization chamber, ion optics, the mass separator, the energy filter, and the detector. The energy filter was used to reduce ions' energy dispersion. The resolution and sensitivity were not reporting, but several ion peaks such as N^+ , Ne^+ , N_2^+ and Ar^+ could be differentiated.

1.2.3 Portable Linear Quadrupole Mass Analyzers

Bench top quadrupole mass spectrometers are the most common type of mass spectrometer in chemical analysis labs due to their low cost and reliability. Most GC-MS instruments use linear quadrupoles. Quadrupole mass spectrometers can operate at relatively higher pressure e.g. 10^{-6} Torr than magnetic sectors and TOF mass analyzers. With size reduction, quadrupole mass spectrometers may work at even higher pressure such as milliTorr range. At the same time, the rf circuit also becomes simpler because of lower voltage requirement. Thus, miniature quadrupoles become very attractive candidates for miniature mass spectrometers.

Typical quadrupole mass analyzers consist of four equally spaced cylindrical rods with an inscribed radius of $r = 1.1487 \times r_0$ (r_0 = rod diameter), as shown in Figure 1-7.³⁰ Both rf and dc

voltages are applied on these rods. The opposing rod pairs are connected electrically together. The adjacent rods have opposite polarity. At a certain rf and dc voltage, only ions with a certain m/z have stable trajectory and can reach detector. Other ions are filtered and neutralized at the rods. The stability equation of ions in quadrupole mass analyzers is explained with Eq.(5). V is the amplitude of rf voltage; q_x is Mathieu stability parameter ($q_x=q_y$); ω is the angular frequency of rf voltage; r_0 is the radius of quadrupole rods. A mass spectrum can be obtained by increasing the amplitude of the rf and dc voltage while keeping the ratio of rf and dc voltage constant.

$$m/z = \frac{2V}{q_x \omega^2 r_0^2} \quad (5)$$

Figure 1-7 Schematic of rods in a quadrupole mass analyzer.

A MicroQuad has been reported that was made from borosilicate glass by Taylor's group at University of Liverpool.^{31, 32} Each micromachined rod of this quadrupole mass analyzer was 30 mm in length and 0.5 mm in diameter. A commercial VG ANAVAC was used as an ion source and a Faraday plate collector as the detector. An rf circuit was developed for operation at 6 MHz. The best resolution was shown 2.7 u at 10% peak height for ion m/z 40. Later, this group used a portable quadrupole mass spectrometer-Pfeiffer QS422 to monitor volatile compounds exhaled by anaesthetized patients.³³ The results showed that the volatile anaesthetic and respiratory gases can be measured simultaneously even at extremely low concentrations (several ppb). Another quadrupole mass spectrometer with square electrodes were fabricated using MEMS technology reported by Taylor's group.³⁴ Even if the quadrupole field was far from ideal, the performance of this QMS was comparable with that of hyperbolic and circular electrodes in stability zone 1.

With decreasing length and radius of quadrupole rods, the sensitivity of quadrupole analyzer also decreases. In order to recover the sensitivity, Ferran et al. proposed to use quadrupole array to increase the ion volume.³⁵ A 4×4 array of rods generated nine quadrupole filters because adjacent quadrupole can share common electrodes. Both rf and dc voltages were reduced to obtain constant field strength when distance of adjacent rods is smaller. Thus power saves a lot. For example, the 16-rod array save 95% power compared to a single quadrupole with the same total cross section and aspect ratio.³⁶ Higher rf frequency was needed to keep the same

resolution. Krypton isotopes with m/z 78, 80, 82, 83, 84 and 86 were tested with $FWHM$ of 0.75 amu at 14 MHz. The sensitivity was in sub-ppm range and the maximum detectable mass was about m/z 300. Sample introduction system was still a problem for this quadrupole array. A single ionization source can be pointed at one analyzer of the quadrupole array. This would affect the overall sensitivity due to ion diffusion.

Another miniature quadrupole analyzer, with 35 mm long rods and $r_0=0.5$ mm, machined using MEMS techniques and operated at an rf frequency of 6 MHz, has been designed.³⁷ The photograph of this miniature analyzer is shown in Figure 1-8. The whole instrument weighs 14.9 kg and can be stored in a rugged plastic case. This instrument consumed power of 45 W on average and pumps consumed 30 of 45 W. Solid phase microextraction was used as sampling method. Figure 1-9 shows the mass spectrum of butyl mercaptan (with $FWHM$ 1.3 u) compared with library spectrum. The detection limit can reach 5 ppm for a 15 second sampling period.

Figure 1-8 (a) Photograph of a miniature quadrupole mass filter and (b) scanning electron microscope image of the miniature quadrupole mass filter. Image reproduced from Reference 34.

Figure 1-9 Mass spectrum of butyl mercaptan sampled from headspace above aqueous solution. Spectrum reproduced with permission from Reference 34.

In summary, quadrupole mass analyzers can be easily miniaturized due to its simple structure and low cost. The miniaturized quadrupoles can work at higher pressure and consume less power. The reduction of sensitivity can be regained using array quadrupoles. MEMS techniques can be used to fabricate micro-scale electrodes.

1.2.4 *Portable Quadrupole Ion Trap Analyzers*

Quadrupole ion traps (QITs) are also common mass spectrometers, especially where tandem mass spectrometry is concerned. The principle of operation of QITs is very similar to linear quadrupole mass analyzers. An rf voltage is applied on hyperbolic ring electrode with two ground hyperbolic end caps forming the quadrupole field as shown in Figure 1-10. At a certain rf voltage, ions of wide mass range above a specific low mass cutoff can be stored in the ion trap.

By scanning the rf voltage, the ions' motion will become unstable and be ejected and detected in order of their mass to charge ratios.

Figure 1-10 Schematic of a Thermo LCQ ion trap mass spectrometer

An ion trap mass spectrometer has many advantages that make it suitable for miniaturization. Firstly, QITs can operate at higher pressure $\sim 10^{-3}$ Torr range compared to 10^{-5} Torr or less for other analyzers. Ions can have better collisional cooling effects in this pressure range, and then ions are manipulated and trapped efficiently. The increased operating pressure makes a small diaphragm pump adequate instead of a large roughing pump. Secondly, QITs can perform tandem MS, so higher degrees of specificity through MS/MS can compensate for loss of specificity because of decreased resolving power, so structural information can be obtained

through MS/MS. Thirdly, the required rf voltage to scan decreases greatly when the size of QIT becomes smaller, as shown in Figure 1-11. For example, in order to scan to a given m/z value, required rf voltage in an ion trap decreases with r_0^2 , so the rf voltage in an ion trap of a radius of $\frac{1}{2} r_0$ is one fourth of ion trap with radius of r_0 . This low rf voltage has a negative effect on the performance. The potential well depth also decreases which may detriment mass resolution of instrument. One way of increasing the potential well depth is to use higher rf frequency that requires higher rf voltage compared to the rf voltage at lower frequency.

Figure 1-11 Schematic to show the relationship between the size of quadrupole ion trap (QIT) and rf voltage. Schematic reproduced with permission from Reference 4.

Kaiser et al have miniaturized a hyperbolic ion trap with inner radius 0.5 and 0.25 cm.³⁸ Mass range of m/z 70,000 was achieved, but with very poor resolution. Small hyperbolic electrodes are difficult to fabricate with high precision, so the researchers focused on a simplified analog called a cylindrical ion trap (CIT). The CIT uses flat end caps and cylindrical ring electrode, as shown in Figure 1-12.³⁹⁻⁴⁴

The CIT is amenable to miniaturization due to its simple structure. One miniature CIT was developed by Cooks' group at Purdue University, which has an inner radius of 2.5 mm and distance of 5.8 mm between the end caps.⁴⁵ A diaphragm pump and one turbo pump were used to obtain a base pressure of 4×10^{-6} Torr, but typically operated at 10^{-3} Torr range in the experiment. Both an EI source and a glow discharge ion source have been coupled with CITs.^{10, 46} Direct leak and membrane introduction inlet systems were designed for sampling. rf Frequency for trapping was 2.0 MHz. Mass spectra were obtained in mass selectively instability scan mode. A mass to charge range of m/z 250 was achieved with unit mass resolution. Later, a membrane introduction system was developed to analyze volatile organic compounds in human breath.⁴²

Another CIT, with $r_0=5$ mm and $z_0=5$ mm, was fabricated with a laser induced acoustic desorption ionization source.^{47, 48} Only one roughing pump was used to obtain vacuum around 50 mTorr. A charge detector was used to detect cells and microparticles. In order to improve sensitivity, another micrometer-scaled CIT array was constructed in tungsten on silicon substrate by Cooks' lab.⁷ It consists of 10^6 CITs with internal radii of 1 μm , which can trap at most one ion

for each micro CIT. Low rf amplitudes (up to a few GHz) with high frequency (up to a few GHz) were needed to increase the potential well depth. Compared to hundreds of watts power consumed by bench scale ion traps, this ion trap array only consumes tens of Watts. Ramsey et al. have also developed quadrupole ion trap arrays.⁸ They built an array of CITs with radius of 20 μm . 100 MHz rf circuit was used to trap ions with amplitude of 45 V. Xe^+ signal was obtained with very low intensity at pressure of 10^{-4} Torr. The performance of their CIT array was limited by ion detection and amplification system at high pressure and high frequency matching circuit.

Another miniature ion trap with simplified structure, called a rectilinear ion trap (RIT), has also been developed. RITs normally consist of two pairs of flat electrodes and one pair of flat end electrodes, as shown in Figure 1-12.

Figure 1-12 Evolution of rectilinear ion traps from hyperbolic ion trap and quadrupole, reproduced from reference 49 with permission

RITs have larger trapping volumes and better sensitivities than CITs. RITs can also tolerate more space charge repulsion effects, and can have larger dynamic range. Cooks' group has conducted significant research on developing miniature RITs. One shoebox-sized RIT was reported as Mini 10 with weight 10 kg.⁴⁹ Both EI and glow discharge ion sources can be coupled to this RIT. An air core tuning circuit was built to provide rf to this RIT at around 100-350 kHz. This Mini 10 was characterized with mass range of m/z 500, limit detection of 50 ppb and unit

resolution. The power consumption is 70 W. Later, the same group developed a new version Mini 11 in which multifunctional/minimalist was used as a principle of design.⁵⁰ Multiple ionization sources such as glow discharge electron ionization (GDEI), electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) and desorption electrospray ionization (DESI) can be coupled to Mini 11. Different parts including ionization source, ion transfer interface and pressure measurement device were minimalized through the philosophy-low power, simple design. The whole instrument now weighs 5.0 kg and measures 22 × 12 × 18 cm. The consumed power is less than 35 W. A mass range of m/z ~1500 was demonstrated with protein molecules. The limit of detection was found to be parts-per-billion range. Then Cooks group developed another RIT with interelectrode distances of 10 by 8 mm (x by y) for operation at mTorr range.⁵¹ Two-stage differentially pumped system was used to maintain the vacuum. Ions were guided by an ion funnel and cooled by a square quadrupole before entering RIT. X-Y plate electrodes were applied with rf 1.08 MHz of 180 degree out of phase. The performance of this RIT was investigated at different pressure range from 1-50 mTorr. The results showed resolution decreased with increasing pressure. A peak at m/z 1522 had a peak width of m/z 5 (FWHM) at 50 mTorr. CID (collision induced dissociation) efficiency was improved at around 50 mTorr.

Another type of ion trap – a toroidal ion trap mass spectrometer – was developed as a compact miniature ion trap.^{52 53, 54} Lammert et al built a toroidal ion trap by edge rotation of an

ion trap as early as 2001.⁵⁴ Larger ion storage capacities can be obtained in toroidal ion traps than in traditional three-dimensional quadrupole ion traps. But, resolution is worse due to the introduction of nonlinear fields by the edge rotation. Further simulations optimized the geometry. An asymmetric toroidal ion trap was built with unit mass resolution. Later, a smaller version of toroidal ion trap, only 1/5 of previous version, was constructed by the same group.⁵³ The similar ion storage capacity was maintained even with reduced dimension. Further simplified geometry of toroidal ion trap was developed by Austin et al.⁵² It was based on edge rotation of cylindrical ion trap. It was comprised of two rf electrodes and an AC electrode that surround a central electrode. Better resolution was reported for sample toluene.

In summary, ion traps are very suitable for miniaturization due to that high-pressure tolerance and tandem MS capabilities. Ion traps with different geometries, such as quadrupole mass filters, RITs, CITs and toroidal ion traps have been investigated so much that they are now commercially available by several different companies.

1.3 Commercially Portable Mass Spectrometer

The commercially available portable mass spectrometers are summarized in Table 1-1. All these portable mass spectrometers share two common features. Firstly, they all use two stage pumps, either a turbo molecular pump or ion getter pump and a roughing pump. Secondly, they require high voltage. For these quadrupole and ion trap, they need high voltage rf circuit with a tuning circuit. The TOF needs large dc voltages and a large pulsed dc voltage. It is widely

recognized that requirement for high vacuum and high voltage prevent the true miniaturization of mass spectrometer. Here we developed a portable Loeb-Eiber mass filter, which can work at relatively high pressure (~ 1 Torr) and require low rf voltage (lower than ~ 30 V_{PP}). More details about our Loeb-Eiber mass filter will be in the following chapters.

Table 1-1 Manufactures of portable mass spectrometer commercially available in U.S.

Name	Manufacturer						
	Bruker	Constellation Technology	ESS Ltd	Inficon	ICX Griffin Analytical	Kore	Microsaic
	MM 2	CT-1128	Ecosys-p	Hapsite	400	MS 200	ChemPac
Mass analyzer type	Quadrupole	Quadrupole	Quadrupole	Quadrupole	Cylindrical Ion Trap	Time of Flight	Chip-based Quadrupole
Sample introduction	Membrane	GC	Membrane, Direct	Direct vapor, GC	GC, Membrane or SPME	Membrane	GC, Membrane, SPME
Ion source	EI	EI	EI	EI	EI	EI	EI
Mass range	0-520	1.6-800 (0.1 steps)	—	1-300	50-425	1-1000	1-400
Resolution (w_b @ max m/z)	1	1	—	1	1	1	1
Acquisition speed (amu/sec)	7,200	10,400	—	1,000	10,000	20 kHz*	10,000
Size (cu ft)	2	3.8	3	1.2	4.5	1.4	1
Weight (lbs)	77	75	—	35	85	44	31
Vacuum pumps	Ion getter	1x rough, 2 x turbo	—	Ion getter	1 rough, 1 turbo	Ion getter	"two-stage"
Power consumption	External 24 V DC	300 W sustained	—	150 W (~3 hrs)	130-250 W (w/ GC)	~6 hrs	~10 hrs
Price (\$1000)	--	140	—	—	50	74	--

#excludes fore pump; *spectra per second

CHAPTER 2: HISTORY BACKGROUND AND BASIC THEORY OF THE LOEB-EIBER FILTER

2.1 Introduction

In 1930s, Loeb built a filter instrument which could filter electrons in an oxygen plasma and allow heavier ions to pass.^{55, 56} In 1960s, Eiber improved the design to resolve three ions, O^- , O_2^+ , O_3^- .^{57, 58} The filter Loeb and Eiber developed can be categorized as energy balance mass spectrometer or linear periodic acceleration mass spectrometer.⁵⁹ To honor these developers, this instrument is called Loeb-Eiber mass filter. There are no reports using this method to differentiate ions since Eiber's work in the 1960s. Eiber's demonstrated mass resolution at about 10 for oxygen ions, which, even without advanced electronic circuit, cutting-edge fabrication and optimization method, has similar resolution to current ion mobility spectrometers. The Loeb-Eiber mass filter has several unique advantages over current miniature mass spectrometers. Firstly, it can work at high pressures such as 1.7 Torr, so can operate without a turbo pump. Secondly, it does not need high voltage radio frequency (rf) power source; less than 30 Volt V_{pp} should be enough to filter ions up to $m/z \sim 150$. Thirdly, the size of the Loeb-Eiber mass filter can be fabricated very small (around 25 μm thick $\times$ 1 cm long $\times$ 1 cm wide). All these advantages make it ideal for making portable mass spectrometer.

The core part of Loeb-Eiber mass filter consists of an array of fine wires, like the strings of a harp. The odd numbered wires connect with an rf voltage, and the even numbered wire

connects with another rf voltage that is π radians out of phase. In Eiber's working device, each wire had a diameter of 31 μm with a gap of 9 μm between adjacent wires in Eiber's mass filter. The ions will oscillate when they go through the mass filter, as shown in Figure 2-1.

Figure 2-1. Schematic diagram of two adjacent wires, reprinted from reference 54 with permission.

According to Eiber, the ions' oscillating amplitude follows this equation⁵⁸

$$A = -\frac{qE}{m\omega^2} \quad (6)$$

where A is half of the distance between adjacent wires, E is electric field strength between adjacent wires, ω is the angular frequency $2\pi f$, m is mass of an ion, and q or z is the charge of an ion. Because E can be expressed by

$$E = \frac{U}{d} \quad (7)$$

where U is the voltage in between adjacent wires and d is the distance between adjacent wires, as shown in Figure 2-1. By combining Eq. (6) and Eq. (7), the required rf voltage to filter a certain type of ions with m/z is

$$U = -\frac{d^2 \omega^2 m}{2z} \quad (8)$$

Eiber only gave this equation without derivation which is given here to know its derivation.

2.2 Mathematical Derivation

Assume one ion moves between two parallel plates, shown in Figure 2-2. The initial position of the ion can be anywhere between two parallel plates. Its initial coordinate (x,y) is assumed to be (0,0).

Figure 2-2 Schematic of ion's motion in two parallel plates with voltage U

According to Newton's Second law, the force F is a function of acceleration a of an object:

$$F = ma \quad (9)$$

where m is the mass of the object.

For an ion in an electric field, the electric field force is:

$$F = Eq \quad (10)$$

where E is the electric field strength and q is the charge on the ion. If acceleration is $\frac{d^2y}{dt^2}$, and the

ion has some motion in the y direction, then:

$$F = m \frac{d^2y}{dt^2} \quad (11)$$

We can combine (10) with (11) to arrive at:

$$Eq = m \frac{d^2y}{dt^2} \quad (12)$$

Since E is defined as $\frac{U}{d}$ where U is the applied voltage and d is distance, this formula can

be rewritten as:

$$\frac{qU}{d} = m \frac{d^2y}{dt^2} \quad (13)$$

In the case of a time varying, sinusoidal rf field, the applied rf voltage can be described as $U_0 \cos(\omega t + \varphi)$, where ω is the angular frequency and φ is initial phase angle of rf voltage. Now, (13) can be rewritten as:

$$m \frac{d^2y}{dt^2} = \frac{U_0 q}{d} \cos(\omega t + \varphi) \quad (14)$$

Rearranging (14) gives rise to:

$$\frac{d^2y}{dt^2} = \frac{U_0 q}{md} \cos(\omega t + \varphi) \quad (15)$$

Integrating this second order differential leads to:

$$\frac{dy}{dt} = \frac{qU_0}{md\omega} \sin(\omega t + \varphi) + C_1 \quad (16)$$

And integrating a second time obtain the position at a given time and leads to:

$$y = -\frac{qU_0}{md\omega^2} \cos(\omega t + \varphi) + C_1 t + C_2 \quad (17)$$

At the initial conditions, $t = 0, y = 0$ and $\frac{dy}{dt} = 0$

(16) can be rearranged to show that

$$C_1 = -\frac{qU_0}{\omega d} \sin\varphi \quad (18)$$

Substituting (18) into (17) and rearranging, Eq. (17) can be evaluated for C_2 :

$$C_2 = \frac{qU_0}{md\omega^2} \cos\varphi \quad (19)$$

With these two correction factors, we can evaluate the amplitude of ion motion across any initial condition or phase angle. The complete equation of ions' motion can be written as below with U_0 or E :

$$y = -\frac{qU_0}{md\omega^2} \cos(\omega t + \varphi) - \frac{qU_0 t}{m\omega d} \sin\varphi + \frac{qU_0}{md\omega^2} \cos\varphi \quad (20)$$

or

$$y = -\frac{qE_0}{m\omega^2} \cos(\omega t + \varphi) - \frac{qE_0 t}{m\omega} \sin\varphi + \frac{qE_0}{m\omega^2} \cos\varphi \quad (21)$$

Eq. (21) shows that the trajectory function of ions consists three terms - a cosine term, a linear term and a constant term with time. The trajectory of an ion depends greatly on initial phase. The trajectory is a stable sinusoidal waveform only when initial phase is integral multiple of pi radians because the second term-linear term becomes 0. To clearly show the effect of initial phase angle dependence on trajectory, phase angle of 45 degree intervals between 0-360 degrees

are plotted, shown in Figure 2-3. The plot is obtained at the following conditions: amplitude of radio frequency (rf) voltage is $0.1 V_{pp}$ with a frequency 68 MHz. The distance between two parallel plates is $7 \mu m$. Particles have m/z 16. Only at 0, 180 and 360 degree, the trajectory is shown to be stable standard sinusoidal waveform. For other phase angles, the trajectory either goes downward or upward, which demonstrates a combination of sinusoidal and linear motion.

Figure 2-3. Ions' position at y direction within two parallel plates at different initial phase angles

The discussion above is all based on initial position at y being 0 or equidistant between the two electrodes. The ion can oscillate symmetrically relative to x -axis, only if the initial y value has an offset that is half the amplitude of the oscillation, for example, $0.472\ \mu\text{m}$ under these conditions, as shown in Figure 2-4.

Figure 2-4 Calculated ion's position at y direction with initial phase 0 degree and initial y coordinate at $-0.472\ \mu\text{m}$

2.3 Working Principle

Figure 2-5 shows the ideal transmission current for the Loeb-Eiber mass filter as a function of rf amplitude for an ion beam composed of two ion populations with $2M_1=M_2$. Two groups of ions with m/z 40 (red line) and m/z 80 (blue line) have different oscillation amplitudes, A , between two adjacent rods. The amplitude of ions' motion increases proportionally with the amplitude of the radio frequency waveform. Because the ions arrive at random positions and phase angles between the wires, some ions of a specific m/z will be filtered and some will pass. Therefore, for a given m/z , the ion current decreases linearly with rf amplitude. At a certain rf voltage, all ions of a certain m/z value will be blocked, as shown for 1 V_{pp} for the blue line. The total ion current for an ion beam composed of two different m/z ions (e.g. $m/z[A]=2*m/z[B]$) will go through an inflection point when the smallest m/z ion is blocked. This example only gives two groups of ions. If n groups of ions were present (where $n>1$) in our mass spectrometer, n inflection points should exist. By scanning the rf amplitude, we can find all the inflection points and identify all the ions present in a sample. We also reproduced Eiber's ion current profile for the analysis of oxygen molecular ions at 1.7 Torr, as shown in Figure 2-6. After doing first derivative for the raw data, we can see that the first derivative stay flat when the raw data has a constant slope. A sudden increase of the first derivative occurs when the raw data go through inflection point or discontinuous point. From the second derivative plot, we can see two peaks that correspond m/z 16, 32.

Figure 2-5. Calculated plot to show the ideal behavior when ions of two different m/z values are present in the ion beam transmitting through the filter.

Figure 2-6 Reproduction of Eiber's ion-current profile for the analysis of oxygen ions
a) the raw data, b) the first derivative plot, c) the averaged second derivative.

2.3.1 Selection of rf Frequency

For Loeb-Eiber mass filter to effectively differentiate ions, the selection of rf frequency should follow several criteria⁵⁸:

1. At the highest ion velocity, the transversal oscillation wavelength λ_t should be smaller than $2d$ (d is the gap between the adjacent wires). Therefore, at least one maximum amplitude of oscillation can be found in the effective gap area.

$$\lambda_t \leq 2d \quad (22)$$

According to the wave equation,

$$f = \frac{v}{\lambda_t} \quad (23)$$

Then (22) can be rearranged to be:

$$f \geq \frac{v}{2d} \quad (24)$$

$\frac{v}{2d}$ is called threshold frequency. If the selected frequency does not significantly exceed the threshold frequency, ions are not likely to have an oscillatory maximum as they transmit the wires, so will not be effectively blocked. Another effect is the field inhomogeneity and boundary due to the difference in the cylindrical gap width on the ions'

path is relatively small. Two effects are different spatial phase position of the ion oscillation to the grid plane and the velocity distribution of the ions. All these may cause a rounding of the ideal current curves, as shown in Figure 2-5.

2. If the selected frequency is much higher than threshold frequency, the length of the ion trajectory will be extended and will increase the collision probability within the effective gap area. Moreover, the ions are deflected in part from their transverse movement by collisions, which in turn increase the length of ion trajectory, then this also lead to an increase of the residual current.

2.4 Simulation of Loeb-Eiber Filter

SIMIONTM 8.0 is a powerful software to simulate ions' motion in fabricating scientific instruments. SIMIONTM works by solving the Laplace equation to calculate electrostatic field at every point of space with electrodes as boundary. It can also take space charge effects into consideration by using charge repulsion methods. All these theoretical calculations and numerical simulations can help to predict the best geometry and optimize operating conditions for many different instruments including magnetic mass spectrometers,¹⁵ ion mobility spectrometers,⁶⁰ ion traps.⁶¹ For our Loeb-Eiber instrument, some instrument parameters were also investigated before building and testing.

2.4.1 *Simulated Ions' Oscillation Amplitude vs Calculated Ions' Oscillation Amplitude*

Since we need to simulate ions' motion at μm scale space under very high frequency, it is necessary to verify that the SIMIONTM software can simulate ions' trajectory accurately and be in agreement with our mathematical calculation at very high frequency (VHF) range. Actually, there are some differences between calculation and simulation situation. The first difference is that the simulation assumes ions with certain initial kinetic energy 0.04 eV. The calculated results do not assume a specific initial kinetic energy and the KE can be any value. The second difference is that the time of birth for ions does not correspond with time of rf voltage in SIMIONTM simulation. This means that if we define ions at birth time 0 in SIMIONTM, it does not necessarily mean that ions start to fly at time 0 of rf voltage $U_0 \cos(\omega t + \varphi)$. So we define eight ions in an rf period and try to fly ions several times to find the best results at initial phase angle 0 degree. The best results mean the simulated trajectory stay at the center instead of moving closer to either electrode. Figure 2-7 shows such a simulation graph at 68 MHz. The centered trajectory seems oscillating almost symmetrically with amplitude of 0.944 μm that is exactly the same with the calculated amplitude of 0.944 μm in Figure 2-3. The SIMIONTM trajectory simulations agree qualitatively with the discrete solutions provided in Figure 2-3, i.e. combination at sinusoidal, linear ramp and y-axis offset, depending on time of birth (phase angle).

Figure 2-7. Simulated ions' trajectory between two parallel electrode plates

2.4.2 *Monopolar and Dipolar Mode*

For simulation within dc electric fields, we need to directly draw the electrodes in SIMION™, and then define dc voltage and particle parameters. For rf voltage, we have to use a function called workbench user program that is an ASCII text file in the Lua programming language.

There are two ways to apply rf voltage on the Loeb-Eiber Filter in actual experiments. One is to apply rf voltage on odd-numbered wires and keep the even-numbered wires at ground or a dc voltage. This is called monopolar mode. The electrodes have been drawn and the simulation is shown in

Figure 2-8 (a). The other way is to apply rf voltage on all the wires and make the rf voltage on the adjacent wires 180 degrees out of phase. This is called dipolar mode, as shown in

Figure 2-8 (b). The rf voltage manipulating code (Lua program) was located in Appendix I. Ions in monopolar mode go through more oscillation cycles. Moreover, the rf electric field may extend into the detector and ion source area. By comparison, the dipolar mode can effectively avoid this because the out-of-phase electrodes cancel out at longer distances.

Figure 2-8 Ions' oscillation in monopolar (a) and dipolar mass filter (b) with rf 0.8 V_{pp} and 100 MHz, red, green, and blue color represent m/z 40, 80, 85 respectively.

The simulated filtering ability was also compared between two modes, as shown in Figure 2-9. For each m/z , it has 500 ions that are defined in line sequence along y-axis. For the trajectory calculation to be reliable, the time step size is less than one tenth of the RF period so that the ion can see each rf cycle as it exists. Each dot in Figure 2-9 represents average surviving ions at 17 different times of birth over one rf wave cycle. Two groups of ions with m/z 40 and 80 are plotted in these simulations. As expected, ion transmission for both m/z values decreases with increasing rf amplitude. For ions of m/z 40, there is no significant difference between the two modes. For ions with m/z 80, the monopolar mode can filter ions more effectively in the middle of voltage range, but the cut off voltage is the same if we define cut off voltage as no particle survive. As can be seen in

Figure 2-8, monopolar excitation causes ions to be accelerated and decelerated in the x-dimension by the powered electrode. This velocity altering behavior has the effect of grouping the ions and distorting their arrival times relative to their times of birth. The resulting effect is that in the simulations the ions arrive with a different distribution of arrival phase angles in monopolar vs dipolar mode, so the filtering is slightly different.

Figure 2-9 Simulation of surviving particles in monopolar and dipolar operation modes with initial ion kinetic energy of 2 eV

2.4.3 Effect of Ions' Position on Flight Path of Ions

It is important to determine where to start to fly the ions in the simulations because their positions influence the simulated cutoff voltages. For the y position, we can use the y coordinate of center (as shown in Figure 2-10) of the gap in between two adjacent wires as the position for ions to start to fly. For the x position, we define λ as one mean free path (at 1.7 Torr, O₂, room temperature) away from the center on the right of electrodes (ions move from right to left) in

Figure 2-10. Several different distances are selected to compare the simulated cutoff voltage, 0.5λ , 0.75λ , λ , 1.5λ , 2λ , 2.5λ .

Figure 2-10 Ions' flight path from right to left in SIMION™ with diameter of electrode $25\ \mu\text{m}$ at 1.7 Torr O_2

Figure 2-11 shows how the cutoff voltage changes with distance of ions away from the center of the electrodes. Each dot represents the cut off voltage of nine thousand ions with m/z 32 ranging from a whole oscillating cycle. It was seen that the distance of ions away from center of electrode has no big effect beyond 1.5λ . For distances smaller than 1.5λ , the cutoff voltage becomes bigger when ions are closer to the center of gap (center is defined in Figure 2-10) in between two adjacent electrodes. The cutoff voltages are 0.395, 0.378 Volt at 0.5λ and 2.5λ respectively. The voltage difference is 0.017 V that is a relatively small difference. This

observation is in agreement with expectation. Ions may not go through a complete oscillation cycle when they are close to the electrodes. Thus these ions may need higher rf amplitude to cut off all ions. Ions can go through more than one maximum inside the electrodes when they are far away from the center of the wires. This is why the cutoff amplitude becomes a plateau when distance exceeds 1.5λ . Since our simulated cutoff voltage is always lower than calculated cutoff voltage, all the simulation will be simulated at 0.5λ away from center of gap even if the voltage difference is not large. In addition, this plot also indicates the position of ion source or Einzel lens in front of mass filter has no big influence on the cutoff voltage because the space between Einzel lens and mass filter easily exceed $50 \mu\text{m}$ (2λ).

Figure 2-11 Ions' cutoff voltage variation with distance away from center of electrode

2.4.4 Effect of Initial Kinetic Energy of Ions on Flight Path

Ions' initial kinetic energy plays a significant role in the ions' flight. The KE determines the ions' velocity and number of oscillating cycles inside the mass filter. Thus it is necessary to look into the speed range of ions and its effect on ions' flight path. The velocity of ideal gas atoms or molecules follows a Maxwell-Boltzmann distribution at thermodynamic equilibrium, and can therefore be estimated using the ion mass and temperature. Argon was used as an example to examine its velocity range, as shown in Figure 2-12. At room temperature (298 K),

the most probable, average, root mean square speeds for argon are 352.2 m/s (0.026 eV), 397.4 m/s (0.033 eV) and 431.4 m/s (0.039 eV), respectively.⁶²

Figure 2-12 Probability density function of argon molecules at 298 K, V-mp denotes the most probable speed; V-ave means average speed; V-rms means root mean square speed.

To investigate the effect of ion velocity on mass filtering, we simulated ions with a velocity range from 0.02 eV to 0.12 eV, as shown in Figure 2-13. The cross section of the simulated mass filter was round with diameter of 25 μm and gap of 7 μm . The Y-axis uses a percentile number that is obtained from dividing surviving ions by the total number of simulated

ions. Each dot represents the number of surviving ions at nine times of birth of one rf wave cycle. The cutoff voltage increases with kinetic energy of ions.

When ions have higher kinetic energy, they can go through mass filter faster and are more difficult to filter because they experience fewer rf wave cycles and are less likely to strike on electrode when their oscillatory maximum A is in between the rods. According to Eiber's equation, the cutoff voltage only depends on m/z and rf frequency. For ions with m/z 48, the calculated cutoff voltage is $0.92 V_{0p}$ according to Eiber's equation. Eiber's experiment⁵⁷ also indicates $0.85 V_{0p}$ that is very close to theoretical value. The simulated cutoff voltage in SIMIONTM is 0.32, 0.46, 0.64, 0.8 V_{0p} that correspond to different kinetic energy, as shown in Figure 2-13. It looks like we may need higher kinetic energy to reach calculated cutoff voltage. But Maxwell-Boltzmann probability density indicates that the most probable speed, rms speed and average speed for m/z 48 are 322.36 m/s (0.026 eV), 394.8 m/s (0.039 eV) and 363.7 m/s (0.033 eV) respectively. Almost no ions exist with higher than three times probable speed (0.078 eV). The possible explanation is that ions do not follow Maxwell-Boltzmann distribution at Eiber's experiment condition because of existence of weak electric field. At electric field strength of 17 V/cm and pressure of 1.7 Torr, ions' KE distribution needs to be further investigated.

Figure 2-13 Ions' transmission percent versus rf voltage (V_{op}) at different ion kinetic energies for m/z 48 at 68 MHz filter frequency

Eiber's equation also indicates that the ions' transmission current should decrease with a constant slope when increasing rf voltage if only one pure substance exists. But in our simulation, the transmission current curves first go down with a constant slope, then decrease with a steeper slope close to the threshold or cutoff voltage. This reason for the change in slope is probably that ions are reflected when increasing rf voltage to certain value. For example,

considering ion flight simulations for ions of m/z 48 at 0.04 eV, as shown in Figure 2-14, when the rf amplitude reaches 0.42 V, the transmitted ion curve starts to go down steeper and the percent of reflected ion starts to increase because the kinetic energy of ions is not high enough to overcome the electric field force in the transversing direction of the mass filter. In other words, the ion filtering follows expected behavior, but the reflection of ions causes additional decrease in transmitted ion current when rf amplitude approach cutoff amplitude. Not only the plot at KE 0.04 eV in Figure 2-14 shows the curved line, all plots at different KE in Figure 2-13 show similar trend. With kinetic energy increasing, the curve of ions transmitting mass filter is more like a straight line, as shown in Figure 2-13.

Figure 2-14 Simulated percent of reflected and transmitted ions versus applied rf amplitude at KE 0.04 eV

In reality, Maxwell-Boltzman distribution of ions exist with a kinetic energies instead of a uniform KE, so we sum up three curves with different kinetic energies (0.02 eV, 0.04 eV, 0.08 eV) to provide an aggregate plot, as shown in Figure 2-15. We can see the transmission curve is close to the ideal straight line at lower than 0.3 Volt. There are several choppy segments at 0.3, 0.4, 0.5 Volt which correspond to 0.02, 0.04, 0.08 eV respectively. Clearly, if enough kinetic energies, positions of birth and times of birth are simulated, the ion transmission behavior

follows the predicted behavior, assuming the kinetic energy is low enough to permit sufficient number of oscillations.

Figure 2-15 Average of ion transmission at 0.02, 0.04, and 0.08 eV for m/z 48

In our simulation, we did not consider ion collision. The reason is that we assume ions have a mean free path that is larger than the diameter of mass filter wires. Thus we can simulate ions' oscillation right around the entrance of the mass filter without considering ions' collision.

2.4.5 *Simulated Ions' Cutoff Voltage vs Calculated Cutoff Voltage*

After researching ions' initial KE and position, eight groups of ions were simulated to study the cutoff voltage with variation of m/z , as shown in Figure 2-16. The simulated cutoff voltages are summarized in Table 2-1. All the simulated cutoff voltages are lower than the calculated voltages. In theory, they are supposed to be straight line, but we know that undersampling the distribution of kinetic energies causes non-linear decreases close to the cutoff voltages. We also extend the first segment of transmission curve to obtain the extrapolated cutoff voltage, as shown in Figure 2-17. Even if extrapolated cutoff voltage is larger than simulated cutoff voltage for each ion, it is still much smaller than calculated cutoff voltage. Moreover, the difference between simulated cutoff voltage and calculated cutoff voltage increases with mass to charge ratio.

Figure 2-16. Plot of transmission efficiency for 8 different m/z values. Each data point is the average transmission of nine times of birth across one period of the rf with KE 0.04 eV and distance 0.5λ .

Figure 2-17 Extrapolated transmission curve with rf voltage.

Table 2-1 Simulated, extrapolated and calculated cutoff voltage

m/z	Simulated cutoff voltage V_{0p}	Extrapolated cutoff voltage V_{0p}	Calculated cutoff voltage V_{0p}
16	0.26	0.26	0.37
20	0.29	0.33	0.47
32	0.37	0.43	0.74
40	0.42	0.51	0.93
48	0.46	0.56	1.11
60	0.52	0.64	1.39
80	0.6	0.78	1.86
96	0.64	0.87	2.23

2.4.6 Comparison of Round Cross Section and Square Cross Section Wires

As shown in the equation derived in Chapter 2.2, the Loeb-Eiber mass filter might also use square cross section electrodes or wires. Square wires have many advantages: firstly, it is easy to make uniform electrode with smaller tolerance; secondly, it is easy to make microfabricated chip-based mass filter, and electrodes with smaller size are possible; thirdly, the transmission distance can be increased relative to round wires, thereby increasing the probability of filtering ions. But, it is unknown that which geometry has better performance. To compare

filtering efficiency, ions' oscillation and potential contour with the two different geometries mass filters were studied. Figure 2-18 shows simulated flight path of ions with m/z 32 in both square and round cross section mass filter at $rf=0.6 V_{pp}$, 68 MHz. The same ions can go through more rf cycles in the square mass filter, indicates that ions can be filtered more effectively in square mass filter than round mass filter.

Potential contour lines between two geometries are also compared as shown in Figure 2-19. The electric field in adjacent square electrodes is more like a uniform electric field. Thus ions oscillate with similar amplitude, as shown in in square geometry. For round geometry wires, ions' oscillating amplitude first increase then decrease when they go through the gap.

Figure 2-18 Simulated flight path of ions (fly from left to right) with m/z 32 in both square and round geometry mass filter at rf $0.6 V_{pp}$, 68 MHz. Ions undergoes ~ 11 maxima in square cross-section wires, but only ~ 4 maxima in round wires.

Figure 2-19 Potential contour comparison within both square and round geometry mass filter; square electrode has cross section 25 $\mu\text{m} \times 25 \mu\text{m}$ with gap 7 μm ; round mass filter has diameter of 25 μm with gap of 7 μm .

2.5 Development of Loeb-Eiber Mass Filter

2.5.1 *Summary of First Generation Mass Filter*

The first generation mass filter was built by a contracted company-Precision MicroFab (Philadelphia PA). All the experiments with the first-generation mass filter were done by a previous group member, Derrell L. Hood.⁶³ The mass filter mainly consists of a set of interweaving round nitinol wires and a polyimide support. Lasers were used to etch the polyimide support to form precise grooves within which the wires are seated. In the first generation filter, the wire had a diameter of 75 μm with a gap of 25 μm between the adjacent wires. The transmission efficiency is therefore about 6.25% ($25\% \times 25\%$) because the nitinol wire is spooled on both front and back faces of the polyimide support. The fabrication process is shown in Figure 2-20. The socket connector was inserted into the support to connect with two wires. Figure 2-21 shows final Loeb-Eiber filter array of alternating isolated wires. The resistance was measured as infinity and the capacitance was measured at 5 nF.

Figure 2-20. Photograph of producing a 1st generation Loeb-Eiber mass filter

Figure 2-21. Final Loeb-Eiber filter array of alternating isolated wires

After some experiments using an ion gun, the 1st generation mass filter was found to be shorted. The resistance was found about 110 Ohms. There might be a short between some adjacent wires. To understand where the problem was, a microscope was used to further examine the mass filter. It was found that the wires were covered by polyimide due to sputtering. In addition, the polyimide backbone and wires were damaged due to high ion energy from ion gun. To make the mass filter work properly, a new mass filter need to be designed to tolerate heat,

high sputtering and current. Also an ion source with low kinetic energy is preferable to avoid sputtering polyimide.

CHAPTER 3: THE DEVELOPMENT OF THE SECOND GENERATION LOEB-EIBER MASS FILTER

3.1 Construction

The second generation Loeb-Eiber mass filter was made to have a single array of wires instead of the dual array of the first generation filter. The design is shown in Figure 3-1. This design has increased ion transmission efficiency to 25% from 6.25%. To make the array, one wire was spooled on an etched polyimide support, epoxy-resin held in place, then cut to remove unwanted wires. The process was repeated on a smaller polyimide support. Finally, the two-polyimide supports were positioned together to create the interleaved array. Each wire was attached to both ends of the rectangular platform. This can avoid electrical connection problems due to distorted grooves. In addition, due to the resistance of wire ($76 \mu\text{Ohms/cm}$), there was a time lag for high frequency electrical signal to go from one end of the wire to the other end of the wire in the first generation mass filter. In the second generation, each wire is attached to a connection bar that then connects with a connection socket by a piece of short wire. This arrangement ensures instantaneous electrical signal transmission. However, we also experienced some problem with this mass filter. The connection wire that was soldered onto the connection bar was not very reliable. The electrical connection worked for a while, but the connection wire became loose and unreliable after months of testing. It was very difficult to solder it back on the connection bar in our lab because of the restricted access.

To assess the integrity of the mass filter, we measure its resistance and capacitance, as shown in Figure 3-2. If the resistance is infinity and capacitance is around 70 pF (for the second generation mass filter), the mass filter is considered functional. If the resistance shows infinity and capacitance shows zero, either the even or odd numbered wires have a connection problems.

Figure 3-1. Computer generated image of the 2nd generation Loeb-Eiber mass filter. The round wires have a diameter of 75 μm and spacing of 25 μm . Red lines represent odd numbered wires, which are wound on the large insulator. Blue lines represent even numbered wires, which are wound on the smaller insulator.

Figure 3-2. Photo of the second-generation mass filter

According to the principles described in Chapter 1, we can calculate the operating frequency for this generation mass filter. The root mean square speed for argon is 435 m/s at 300 K. The distance between two adjacent wires is 25 μm . In order to obtain one oscillation peak in the effective area, f has to satisfy the following equation:

$$f_0 \geq \frac{v}{2d}$$

Thus, f_0 has to be larger than 8.7 MHz. Considering that ions may fly through the gap between two adjacent wires at higher speed (twice the rms speed), it is necessary to double the calculated frequency. Thus, the minimum operating frequency should be 17.4 MHz for argon. Since the operating frequency is dependent on the speed or mass of ions, ions with smaller m/z

have larger f_0 . Therefore, it is necessary to calculate the operating frequency for the small molecules. For example, in Eiber's paper, he tried to resolve three ions O^- , O_2^+ and O_3^- . Then he used O^- to calculate the minimum operating frequency, about 68 MHz. In our experiments, we are going to use helium, argon, neon. Thus we use helium to calculate its operating frequency about 55 MHz.

3.2 rf Circuitry Issues

For the first generation mass filter, Derrell Hood directly applied arbitrary function generator (AFG) to electrical feedthrough pins of chamber then connect to the mass filter. The feedthrough pins that connect both rf and dc power supply were all mounted on the same metal plate and they were very close to each other, as shown in Figure 3-3(a). The voltage was not measured on the mass filter after the AFG was applied to the mass filter. Derrell assumed the voltage on the mass filter should be the same as the output of the AFG. As a result, he can only demonstrate the ability of first generation mass filter to pass or block ions at low frequency square wave (1 KHz). He could not get the expected filtering effect at higher than 1 MHz modulated sine waveform. With our in-depth knowledge of this project, we started to realize that the function generator displays might not be the same with the real voltage on the mass filter. For example, we used two oscilloscope probes to measure the voltage on the mass filter inside the chamber. The measurement showed there was significant attenuation from the function generator to the mass filter. Thus, it is very necessary to build a matched rf circuit to transmit maximum

voltage from the function generator to the mass filter. This circuit should not only transmit rf voltage, but also transmit dc voltage to make ions move in a continuous electric field gradient. This circuit should be able to work up to 30 V_{pp} at around 70 MHz.

In addition to adding a tuning circuit, it was necessary to modify the position of rf transmission cable through vacuum chamber to avoid the effect of nearby conductor on rf electrodes. rf electrodes are separated from dc electrical feedthrough pins to go through another metal plate right across the chamber from the previous electrical feedthrough, as shown in Figure 3-3 (b). In addition, a short piece of BNC cable was used to transmit rf instead of a Kapton® wire inside the chamber.

Figure 3-3 The position of dc and rf electrical feedthrough before (a) and after modification (b).

3.3 Creating Radio Frequency Voltage

3.3.1 *Circuit Configuration*

A schematic flow for generating rf voltage to the Loeb-Eiber filter is shown in Figure 3-4. It consists of several components: generation and modulation of rf signal, dc coupling and an impedance matching circuit. Typically, the generation and modulation of rf signal is achieved by a function generator (AFG 3252, Tektronix). One rf amplifier can be used to amplify voltage of rf signal from the function generator because a typical function generator can only provide a maximum signal of 5.0 V_{pp}. In our experiment, a commercial broadband power amplifier (Electronic Navigation Industries, Rochester, NY model 525LA) was used. A dc power supply, which can provide dc voltage offset to mass filter through resonant tank circuit, is also required. The last component is tuning circuit that consists of a center tap transformer. The rf signal was measured by an oscilloscope coupled with a low capacitance probe P6158 (Tektronix, Beaverton, OR).

Figure 3-4 Schematic flow for the generation of rf voltage for Loeb-Eiber mass filter.

3.3.2 Very High Frequency (VHF) Issues

The normal working frequency for our mass filter is from 30 to 100 MHz. Several variables, including parasitic inductance, parasitic capacitance and skin effect become important at these high frequencies, even dominant at some cases, when designing rf circuit (a good cutoff is 30 MHz). These issues may greatly attenuate incoming signal. Thus, it is necessary to discuss these VHF issues. First, we need to explain the different frequency range. As shown in Table 3-1, Medium frequency (MF) radio frequency is generally considered to range from 0.3 MHz to 3 MHz. Typical quadrupole and ion trap mass spectrometers work in this range. High frequency (HF) rf ranges from 3 to 30 MHz with a wavelength 100-10 m. The next band is Very High Frequency (VHF) that ranges from 30 - 300 MHz with a wavelength 10-1 m. The Loeb-Eiber mass filter normally works at this range.

Table 3-1 Defination of frequently used terms

	Frequency Range	Wavelength Range
Audio Frequency (AF)	20 Hz – 20 kHz	15,000,000 – 15,000 m
Low Frequency (LF)	30 kHz – 300 kHz	10000 – 1000 m
Medium Frequency (MF)	0.3 MHz – 3 MHz	1000 – 100 m
High Frequency (HF)	3 MHz – 30 MHz	100 – 10 m
Very High Frequency (VHF)	30 MHz – 300 MHz	10 – 1 m
Radio Frequency (rf)	3 kHz – 300 GHz	100,000 – 0.001 m

3.3.2.1 Parasitic Inductance

The Maxwell equation demonstrates that wires that carrying time-changing current induce varying magnetic field around the wires. This electromagnetic field leads to opposing potential gradient through wire as shown in Figure 3-5. This voltage is proportional to the frequency of the time changing current. This is considered mathematically as effective inductance. Any wire has such effect, including even the leads of resistor and capacitor.

(A)

★ = Any Component

(B)

Figure 3-5 Parasitic inductance generated along a straight wire at VHF. At (A), changing current develop a changing magnetic field which induce a back electromagnetic field (EMF). B shows the parasitic inductance generated with general model.

The inductance of a straight, round and non-magnetic wire can be calculated by the equation below ⁶⁴:

$$L = 0.00508b \left[\ln \left(\frac{2b}{a} \right) - 0.75 \right] \quad (25)$$

where

L = inductance, in μH

a = wire radius, in inches

b = wire length, in inches

$\ln$ = natural logarithm ($2.303 \times \log_{10}$).

For example, a piece of wire (#24 gauge) with length of 2 inches (50.8 mm) has an inductance of 45.57 nH. The inductive reactance is 0.286 Ohms at 1 MHz, and 20 Ohms at 70 MHz. This inductance can be treated as series inductor to the component. It is not evident at medium frequency, but quite evident at VHF. This is why rf circuit design at VHF range requires lead length and interconnecting wire as short as possible.

3.3.2.2 *Parasitic Capacitance*

The Maxwell equation also tells us that time-varying voltage generates displacement current between two points. This displacement current comes from the propagation of an electromagnetic field. The displacement current is different from induction current. The amplitude of the displacement current is proportional to the frequency of the voltage.

The displacement current is mathematically considered as a capacitor. This parasitic capacitance sometimes is also called stray capacitance, a general term caused by voltage difference on two adjacent metal surfaces. It is parallel with the corresponded component, as shown in Figure 3-6. The total impedance can reach a maximum at a certain frequency that is

called self-resonance frequency. Below this frequency, the total impedance is inductive. Above this frequency, the total impedance is capacitive. Its value ranges from nF to pF. Below VHF, the parasitic capacitance is viewed as open circuit (infinity resistance). In our tuning circuit at VHF, any leads, interconnecting wires and air core transformers all possess parasitic capacitance.

Figure 3-6 (A) Parasitic capacitance generated by inductor coil. (B) Self resonance can be reached at a certain frequency for a normal coil at VHF, reproduced with permission from reference 59.

3.3.2.3 A General Model

From the analysis above, a single capacitor or inductor can be considered as an RLC model, as shown in Figure 3-7. Figure 3-7(A) shows a general model for a capacitor. L_s and R_s

are added effects, thus are in series with the capacitor. R_p is the leakage resistance that is caused by the non-ideal medium in the capacitor. The ideal medium in a capacitor is vacuum and no dc current goes through. In fact, our capacitors are filled with air in which atoms may exist. Thus, leakage current may form and it can be modeled as leakage conductance G_L or leakage resistor R_p . It is the leakage current that enables a small dc current to pass in real air capacitors. As a comparison, Figure 3-7(B) shows a general model of an inductor in which C_p and R_p are parasitic, so they are parallel with the inductor.

Figure 3-7 A general model of a capacitor (A) and an inductor (B) at VHF.

In these RLC models, the capacitor and inductor may have a self-resonance frequency that is close to its expected operating frequency in VHF range. If the operating frequency is larger than the self-resonance frequency for an inductor, it may become capacitive. A capacitor may appear inductive above the self-resonance frequency. For example, a capacitor with 10 pF

may have a 28 mm (1.1 inch) lead on each side. According to equation 3-1, the parasitic inductance of the lead is

$$L=0.00508 \times 1.1 \times (\ln(2 \times 1.1/0.013)-0.75)=24.48 \text{ nH}$$

The resonance frequency would then be 318.3 MHz for this 10 pF capacitor. If the capacitor were 200 pF, the resonance frequency would be 71.2 MHz.

Figure 3-8 A regular commercial capacitor with 10 pF.

It is difficult to calculate the parasitic effect by hand in a VHF circuit. CAD (computer aided design) software such as PSpice is necessary to simulate these complicated circuits, such as PSpice. These calculations are only used as rough guidance because there are some other factors that may also play a significant role such as orientation of leads, shielding of wires and so on.

3.3.2.4 Skin Effect

The resistance of a conductor to dc current is different to rf. The Maxwell equation indicates that rf current tends to conduct at the surface of a conductor. The depth of conducting layer is proportional to its wavelength. This phenomenon is called the skin effect. By rule of thumb, it is not important below 1 MHz, but becomes significant above 1 MHz.

An equation can be used to calculate the cutoff frequency to consider skin effect.

$$f = \frac{124}{d^2} \quad (26)$$

f is cut off frequency (unit is MHz), d is the diameter of the conductor (unit is mil or 0.001 inch).

The rf resistance increases 3.2 times when the frequency increase one decade from cut off frequency. For a piece 5 cm length of normal wire (eg. #24 AWG), the dc resistance is

$$R_{dc} = (2/12) \times (25.67/1000) = 4.28 \text{ m}\Omega$$

The cutoff frequency is

$$F_{cutoff} = 124 / 21.3^2 = 0.2733 \text{ MHz}$$

$$\text{The rf resistance is } R_{rf} = 4.28 \times 3.2 \times \log(100/0.2733) = 21.0 \text{ m}\Omega$$

Again, the ARRL handbook⁶⁴ suggests using this calculation qualitatively because it is only an approximate calculation. It only tells us whether it is necessary to ignore the skin effect or not.

3.3.3 *Tuning Circuit Design*

An rf voltage can be provided to a load by a transformer or a tuning circuit that is connected to an arbitrary function generator. Because a dc offset is also required in our mass filter, a dc offset also needs to be built into the circuit. Therefore, a center tap air core transformer is needed in the tuning circuit to transmit both rf and dc voltage. An air core transformer is a type of linear transformer in which the current is proportional to the mutual inductance.⁶⁵ Actually, the core of linear transformer can be air, plastic, Bakelite or wood, as long as the permeability is kept constant.

Before making a transformer, it is necessary to simulate the rf tuning circuit to understand the factors that influence the performance of the circuit. We also need to determine turns of primary and secondary coil. There are two theories for us to consider, one is impedance matching theory, and the other one is resonant tank circuit theory.

3.3.3.1 PSpice Simulation

To make a transformer, we have to know the inductance of both the primary and secondary coils must be known. One can determine the inductance of a secondary coil using resonance theory or impedance matching theory. It is unknown whether the inductance of primary coil influences the resonance frequency and amplitude of secondary coil through mutual inductance. Thus, an analog circuit simulation program called PSpice is used to study the influence of these factors.

Unfortunately, there are no center tap air core transformer in PSpice. So our desired circuit cannot be modeled using pre-existing features in PSpice. However, our desired center-tap air core transformer can be represented using three mutually coupled inductors with a linear element K ,^{66,67} as shown in Figure 3-9.

Figure 3-9 PSpice program simulating a transformer resonant circuit, V3 is power supply, T1 is coax cable with characteristic impedance 50 ohms, C1 represents our mass filter.

The inductance of the primary coil (L_1 in Figure 3-9) of an air core transformer is varied from 1 to 87 nH to research the voltage at the node 2, one polarity of mass filter wires. The inductance on the secondary coil is kept constant at 87 nH. From Figure 3-10, the voltage at the node 2 of the mass filter decrease when increasing the inductance on the primary coil. The voltage at node 2 can reach 6.6 V at LC resonance, which is six times larger than power supply voltage, with primary coil 1 nH. Thus, we should make primary inductance as small as possible to make a step up transformer.

Figure 3-10 Voltage change on the secondary coil with different inductance of primary coil while keeping the secondary inductance constant (87 nH) for frequency = 68 MHz.

We also need to note that PSpice only simulates the ideal situation. The PSpice does not consider the skin effect and eddy current loss attached with inductors.⁶⁸ These factors may cause the actual Q of a physical inductor to decrease when the frequency is higher than a threshold. We can only use PSpice as a rough guide.

3.3.3.2 Impedance Matching Circuit Design

During the design of the impedance matching circuit, two aspects need to be noted, 1) velocity factor (VF) and characteristic impedance. The transmission lines used in our experiment

are coaxial cables, such as RG-58. Basically, it consists of an inner conductor and a concentric outer conductor that is often a woven shield braid. The current that travels in the outer layer can cancel the energy that runs in the inner conductor. Then there is no energy radiation. 2) the rf waveform is supposed to travel with light speed in vacuum space. But, in reality, waveform runs in the conductor which makes travelling speed lower than speed of light. The ratio of velocity of waveform in the coaxial cable to light speed in free space is called velocity factor.⁶⁴ For the RG 58 cable in our experiment, the VF is 0.66. The coaxial cable is equivalent to a circuit shown in Figure 3-11. The inductor indicates the inductance of a short piece of conductor. The capacitor indicates the capacitance between adjacent inductors.

Figure 3-11 Equivalent circuit of an infinitely long lossless transmission line.⁶⁴ Reproduced with permission from reference 64.

The characteristic impedance is an important parameter of a coaxial cable. The characteristic impedance can be expressed in the following equation; L and C are the inductance and capacitance per unit length of line.

$$Z_0 = \sqrt{\frac{L}{C}} \quad (27)$$

The coaxial cables with different models have different characteristic impedance. For example, RG-58 has a characteristic impedance of 50 Ohms. RG-59 has a characteristic impedance of 75 Ohms. If a coax cable terminates with a resistive load that is equal to the characteristic impedance, this is a matched line or flat line because the voltage distribution along this line is constant or flat. The resistive load will absorb all the energy from source. If the load is not equal to characteristic impedance, such as a resistor in series with a capacitor, this is a mismatched line. Some of the power will reflect back to the function generator. The amount of reflected power and absorbed power depends on the difference between characteristic impedance of coax and load impedance.

The discontinuity between coax cable and function generator will make the signal go back to load again. Thus the reflected signal will go back and forth, then decay to nothing. The combination of forwarding waveform and reflecting waveform forms the standing waveform. The ratio of maximum peak voltage anywhere on the line relative to minimum voltage is voltage standing wave ratio (SWR).

Figure 3-12 A general model for a coax cable with a certain impedance.⁶⁴ E_g is a function generator, R_g is the internal resistor of the function generator, R_a is the resistive load, X_a is the capacitive or inductive load.

The ratio of reflected voltage to forwarding voltage is voltage reflection coefficient.

$$\rho = \frac{Z_a - Z_0}{Z_a + Z_0} = \frac{(R_a \pm jX_a) - (R_0 \pm jX_0)}{(R_a \pm jX_a) + (R_0 \pm jX_0)} \quad (28)$$

Z_a is load impedance, R_a is resistive component of load, X_a is reactive component of load, Z_0 is line characteristic impedance, R_0 is the resistive component of line, X_0 is the reactive component of line.⁶⁴

Most transmission lines are almost completely resistive. This means that $Z_0=R_0$ and $X_0=0$, and Eq. (28) can be simplified with following equation:

$$|\rho| = \sqrt{\frac{(R_a - R_0)^2 + X_a^2}{(R_a + R_0)^2 + X_a^2}} \quad (29)$$

In our original experiments, we applied the function generator directly to our mass filter through an RG-58 coax cable ($R_0=50$ Ohms). However, our mass filter has a capacitance 200 pF, at the normal operating frequency 68 MHz, our mass filter should have an impedance at $R_a=0$ and $X_a=11.7$ Ohms. The reflection coefficient is therefore 1.0. Actually, the reflection coefficient stays at 1.0 if our load is reactive regardless of R_0 . It means that 100% waveform reflect back to function generator. This also explains why Derrel did not see filtering signal at high frequency waveform for our first-generation Loeb-Eiber mass filter.

The SWR can be expressed using ρ that is voltage reflection coefficient. If a perfect lossless line is flat or matched, then ρ is 0 and SWR is 1:1.

$$SWR = \frac{1 + |\rho|}{1 - |\rho|} \quad (30)$$

The SWR value can be measured using a reflectometer or power meter. The value of ρ can also be expressed using power. P_r is reflected power and P_f is forward power. The net power between forward power and reflected power is the power applied to the load.

$$|\rho| = \sqrt{\frac{P_r}{P_f}} \quad (31)$$

In our experiments, we tried to measure the forward power and reflected power using our power meter. However, our power meter can only measure as low as 1 W, so the pointer of the power meter hardly moved. We could not find a power meter with a lower range.

Before we designed the impedance matching circuit, it was necessary to introduce reflected coupling impedance from secondary circuit for an air core transformer. This helped us to understand how to build tuning circuit at VHF. Figure 3-13 shows a transformer circuit and its equivalent circuit.

Figure 3-13 The impedance in the secondary coil is reflected back into primary circuit, (A) shows the original circuit, (B) shows the equivalent circuit⁶⁴. E_{AC} is power supply, R_S is internal resistance of the power supply, M is mutual inductance, L_1 is the inductance of primary coil, L_2 is the inductance of secondary coil, R_L is load resistance. Reproduced with permission from reference 58.

The impedance of the secondary circuit in Figure 3-13 (A) is

$$Z_s = \sqrt{R_L^2 + X_{L2}^2} \quad (32)$$

Z_s is the impedance of the secondary circuit,

R_L is the load resistance in ohms,

X_{L2} is the reactance of secondary coil.

The effect of Z_s upon the primary circuit is the same with additional Z_p upon primary circuit as shown in Figure 3-13 (B). Z_p is in an enclosure that means it is an imaginary component. The value of Z_p is

$$Z_p = \frac{(2\pi f M)^2}{Z_s} \quad (33)$$

where

Z_p is the impedance introduced into the primary,

Z_s is the impedance of secondary circuit,

$2\pi f M$ is the mutual inductance between the primary and secondary circuit.

Z_p has the same absolute value of phase angle with respect to the impedance in the secondary circuit, but the sign is reversed.

As for our circuit shown in Figure 3-14, the signal source connects to a coax cable, and the coax cable connects with a transformer and a capacitive load. We can add an extra resistor on the primary side and select a proper transformer to make the reflected impedance counteract the primary inductance. Thus, it can reduce the SWR and make a good impedance match.

Figure 3-14 Schematic showing the impedance matching circuit, V1 is signal source, R1 is internal resistor of V1, C1 is our mass filter, M is mutual inductance between primary coil L1 and secondary coil L2. (A) is real tuning circuit, (B) is tuning circuit with virtual reflected impedance

The impedance of the secondary circuit is:

$$Z_s = X_L - X_C \quad (34)$$

The equivalent coupled impedance in the primary circuit is:⁶⁴

$$|Z_p| = \frac{(2\pi fM)^2}{|Z_s|} \quad (35)$$

According to the definition of mutual inductance:

$$M = k\sqrt{L_1L_2} \quad (36)$$

The coupled impedance has to counteract the inductance of the primary coil:

$$X_{L1} - Z_p = 0 \quad (37)$$

In order to counteract the inductance of primary coil, X_L has to be larger than X_C . Then Z_p can be capacitive.

From the equation below, L_2 can be solved,

$$L_2 = \frac{1}{C\omega^2(1-k^2)} \quad (38)$$

It seems that there is no requirement for L_1 . It can be any value. The k value is normally very low because the leakage reactance is very high for air core transformers. For typical operation of the first and second generation mass filter, we have the following given parameters:

$$C = 70 \text{ pF}, f = 70 \text{ MHz}, k=0.6, L_2 = 115.5 \text{ nH}$$

In order to make a step up transformer, we need to make L_1 as small as possible, such as 1 nH. But in practice, the smallest inductance depends on the size of our transformer core and gauge of magnet wire, for example, 1 turn of a wire with gauge #24 is around 20 nH. We built a

circuit with such inductance. The measured voltage on the mass filter is very low and fuzzy no matter how we tweaked the circuit. The possible reason is that the stray capacitance and parasitic inductance are too large and affect voltage transmission. We therefore tried the second method to build tuning circuit: a resonant circuit.

3.3.3.3 Resonant rf Transformer Design

It is necessary to talk about quality factor (Q) before we introduce the resonant rf circuit. Generally speaking, the quality factor is the ratio of reactance to resistance. Because the series resistance from the secondary winding is less than 1 Ohm in our circuit, as shown in Figure 3-15, the Q really depends on the capacitor or inductor. At 70 MHz, Q of our circuit is larger than 10.

Normally, an air core transformer has a very low coupling coefficient, so the turn ratio is not as important as a magnetic core transformer. The voltage across the secondary coil depends on the mutual inductance and Q of the secondary circuit. In order to improve power transfer, either the primary coil or secondary coil can be made to be a resonant circuit because the reflected reactance can cancel each other. If both the primary and secondary coil are resonant circuits, both windings can be coupled more loosely than a single resonant winding to transfer the same power. In addition, the higher Q value the circuit has, the less mutual inductance it needed to transfer the same amount of power.

Figure 3-15 Constructing a resonant rf circuit that contains both primary and secondary resonant circuit

According to our calculation, our second-generation mass filter (70 pF) needs 78.3 nH inductance to be resonant at 68 MHz. The coil was therefore wound on a plastic screw with a diameter of 0.136 inch. The wire used was #24 that is 0.02567 Ohms per ft. A program called mini Ring Core Calculator (made by Wilfried Burmeister)⁶⁹ was used to calculate the required

number of turns of solenoid inductor. After the turns of the secondary coil of the air core transformer were determined, I choose a different number of turns from the primary coil to compare the results. Then an air core transformer was formed. The two leads of the secondary coil were connected with mass filter. The two leads of the primary coil were connected with the pins of the KF flanged single-end connector and chamber ground respectively. The KF flange connected the AFG through RG-58 coax cable. We tried many transformers with different turn ratios. The voltage measurement on the mass filter was very fuzzy and low, less than 100 mV with input of $5 V_{pp}$ continuous sinusoid waveform at 68 MHz. I exclude all the possible positions that may cause the problem except the KF flange feedthrough. Then I decided to skip this feedthrough and connect AFG directly to transformer then mass filter. The result is much better than before. Figure 3-16 shows the homemade air core transformer with five and six turns on primary and secondary coils respectively. Oscilloscope probes were used to measure the voltage on the connecting pins of secondary coil relative to ground. The result shows 2.71 V and 2.64 V with a phase difference 179.4 degrees. This result indicates that the problem cuasing the fuzzy voltage was from the KF flange single end connector. It was noticed that the shielding layer of BNC coax cable connecting AFG always connected to chamber ground and one side of primary coil was also connected to chamber ground. Actually the shielding of output terminal of AFG itself is not connected to ground. The connection method in Figure 3-16 avoided the shielding layer connecting ground and then generated good result. Therefore it is necessary to replace the

KF flanged single end connector because this flange was designed to connect with chamber ground. It was found that a KF flanged double-end connector satisfied our needs. It has two BNC coaxial connectors on both air-side and vacuum-side. Both the connector bodies are floating shielded which avoids grounding the AFG. A transformer was used to connect the BNC terminal on the KF flange and mass filter, as shown in Figure 3-17. The output measurement on both connection sockets of secondary coil relative to center tap ground showed 2.6 V_{pp} and 179.4-degree phase difference at input 67.4 MHz for 5.0 V_{pp}. Then we added an additional variable capacitor and made it parallel with the primary coil. At a certain capacitance value, the output showed 3.0 V_{pp} and 177.3-degree phase difference for the same input, an improvement of about 0.4 V_{pp}. Since then, we used parallel capacitors on the primary side to make primary resonance circuits when testing different transformers, as shown in Figure 3-18.

Figure 3-16 A home made air core transformer and its result in oscilloscope with input at 67.4 MHz and 5.0 V_{pp}

Figure 3-17 Photograph of a home-made air core transformer with connecting wires

Figure 3-18 Photograph of an air core transformer with a variable capacitor. Transformer schematic is shown in Fig. 3-15.

To characterize the transformer, we scanned the frequency of AFG from 1.0 MHz to 220 MHz and the input amplitude was set to 4.0 V_{pp}, as shown in Figure 3-19. The sweep time was 100 ms. The maximum output voltage was 3.15 V_{pp} at 59.67 MHz. The phase difference between two connecting sockets was about 160 degree. The best phase difference happened at 72 MHz, around 179 degree, but the amplitude was a little lower, about 2.5 V_{pp}, as shown in Figure 3-20.

In theory, the phase difference between two sides of secondary coil should be always 180 degrees independent of frequency. In practice, the amplitudes and phase difference are very sensitive to the position and orientation of center tap wire and core. It is time-consuming to tweak to find the best results at each frequency. This test also indicated that collecting a mass spectrum using frequency sweeps instead of amplitude sweeps is unrealistic in the short term, at least with circuits like this.

Figure 3-19 Amplitude applied to the mass filter (secondary load) using the transformer shown in Figure 3-18 and 4.0 V_{pp} constant amplitude from the AFG into the primary coil.

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Figure 3-20 Amplitude applied to the mass filter (secondary load) using transformer shown in Figure 3-18 and 72 MHz, 4.0 V_{pp} constant amplitude from the AFG into the primary coil.

3.4 Experiments with the Second Generation Mass Filter

3.4.1 Optimization of dc Lens Potential

In Eiber's paper,⁵⁷ he used electric field strength 20 V/Torr·cm for positive ions and obtained fairly good results. But he did not give the data about the distance between lenses. We have to calculate the electric potential on the lens in our assembly if pressure is fixed at around

1.7 Torr. The lenses, mass filter and Faraday cup were arranged as shown in Figure 3-21. The calculated voltages were 108.3 V, 68.6 V, 59.8 V, 51.1 V, 28.5 V, 4.4 V respectively from anode of ion source to the last lens. The outside shielding of the Faraday cup was grounded. Based on the calculated value, we optimized each voltage on lenses and mass filter in experiments. Our goal is to get a signal as intense as possible on the detector. Thus, we watched the signal of detector on an oscilloscope while each voltage was adjusted. At the end of tuning, the signal could not get any better no matter which parameter we adjust. The final operating parameters are shown in Figure 3-21. The calculated voltage for negative mode is shown in Table 3-3. The electrical connection schematic is shown in Figure 3-22. The following experiment all use this electrical connection. A dc power supply provides high voltage for glow discharge. An octo-channel high voltage system that is controlled by a DAQ card (NI PCI 6733) provides voltage to the lenses. The signal on the Faraday cup is amplified through current preamplifier (Model SR570 made by Stanford Research Systems), and then is connected to oscilloscope (Tektronix TDS 3032B) and PC. Another alternative way to acquire signal is using data acquisition card inserted into PCI board instead of standalone oscilloscope. We used NI PCI 6229 to acquire signal, but we cannot average this signal. The reason is that our multifunction DAQ card (PCI 6229) does not support analog triggering. Thus we are not able to trigger the acquisition period from the analog signal itself. This essentially makes it impossible to replace

the behavior of our oscilloscope. In order to acquire signal with integrated PC in the future, we need to buy a DAQ card that supports analog triggering.

Figure 3-21 Picture of assembly of lens, mass filter and Faraday cup

Table 3-2 Calculated dc voltage and experimentally optimized dc voltage at positive mode and 10V/ Torr•cm

	Calculated dc amplitude (V)	Optimized dc amplitude (V)
Anode	108.3	105
Lens 1	68.6	100
Lens 2	59.8	73.8
Lens 3	51.1	55.1
Mass filter	28.5	15.9
Lens 4	4.4	9.5

Table 3-3 Calculated dc voltages in negative mode

	Calculated amplitude (10V/ Torr•cm)	Calculated amplitude (5V/ Torr•cm)
Anode	-54.1	-27.1
Lens 1	-34.3	-17.2
Lens 2	-29.9	-15
Lens 3	-25.5	-12.8
Mass filter	-14.3	-7.1
Lens 4	-2.2	-1.1

Figure 3-22 Electrical connection schematic for experiment

3.4.2 Effects of Operating Pressure on Signals

Our vacuum gauge is not universal and it consists of an ion implanted, piezoresistive, direct force sensor and a thin film Pirani type sensor that is made by Teledyne Hastings (Model 2002). It can provide true pressure measurement for nitrogen, argon, helium and water vapor. For other gases, they have to be calibrated to establish gas thermal conductivity data prior to use. It is not like other vacuum gauges with gas correction factor that is used in the conversion of different gases. For our current vacuum gauge, each gas has a unique curve. There is not a constant difference between two curves.

Argon was first used to test our mass filter to work at different pressures, as shown in Figure 3-23. The glow discharge current was kept at 0.501 mA in current limited mode. The flow rate of argon was varied from 35 sccm to 60 sccm using a flowmeter (Teledyne Hastings HFM-300), depending on the pressure. The rf voltage frequency was set at 66 MHz. The input amplitude of AFG was 70 mV_{pp}, which corresponded to an output amplitude of 7.0 V_{pp}. The amplitude was modulated at a frequency of 250 Hz with depth 100%. The modulation shape was an up ramp (linear ramp from 0 to 7.0 V_{pp} every 4 ms). Data was recorded in the oscilloscope with 10k acquisition data points. Then, the time scale was transformed to rf voltage. Figure 3-23 shows that the signal increases when the pressure decreases. At lower pressure, more ions can reach Faraday cup to generate higher signal because of fewer collision. According to Eiber's equation, the inflection point for our geometry should be around 22.3 V_{pp} for argon. But our rf output only gave 7 V_{pp}. However, we only tested up to 7 V_{pp} because we did not properly calculate some of the conditions at the time.

Figure 3-23 Original plot of Argon signal with ramping rf voltage at different pressures

(oscilloscope is set with a low pass filter 20 MHz, horizontal resolution 10k points, sampling rate 250 KS/s, averaged 512 times)

To compare data from another angle, data in Figure 3-23 was normalized and shown in Figure 3-24. The lowest point is set as 0 and the highest point is set as 1 for every curve of Figure 3-23. It was noticed that ions couldn't be filtered out at up to 7 V_{pp} for pressure of 0.809 and 0.879 Torr. It looks like the signals were filtered out to some extent at around 5 V_{pp} for pressure 0.952, 1.02 and 1.16 Torr. This voltage is far away from our calculated inflection value 22.3 V_{pp} . The reason may be that mean free path at these pressures 0.952 Torr, 1.02 Torr and 1.16 Torr are 56.9 μm , 53.1 μm and 46.7 μm , respectively. These mean free paths are smaller than the diameter of wire of our mass filter – 75 μm . Thus ions' oscillation amplitude equation does not follow Eiber's equation under this situation. In theory, the mean free path should be larger than the diameter, and this requires the pressure lower than 0.72 Torr.

Figure 3-24 Normalized plots of argon signal with ramping rf voltage at different pressures

3.4.3 Effects of Sensitivity of Current Preamplifier on Signals

The current on the Faraday cup was very weak in these experiments, in the nA range. So we used a low-noise current preamplifier (Model SR570 made by Stanford Research Systems) to amplify the original signal. Noise may be introduced and signal may be distorted when amplifying signal excessively. Thus we need to find a proper sensitivity that can amplify signal properly and reflect true signal. The measured argon signal is shown in Figure 3-25 with different sensitivity (settings on the picoammeter). The preamplifier is set at low noise gain

mode that can quickly lift low-level signals above instrument's noise floor. The glow discharge ion source was set at -532 Volt and 0.501 mA. The pressure was 0.808 Torr. The rf input from the AFG was 100.0 mV_{pp} and output around mass filter was measured as 8.3 V_{pp}. The modulation frequency was 500 Hz with up ramp 100%. We can see from Figure 3-25 that the signal increases when increasing the sensitivity. The signal is the highest at the highest sensitivity, 50 nA/V. The signal decreases to half when sensitivity reduces to half, at 100 nA/V. These all agree very well with what we expected.

Figure 3-25 Signal variation of Ar^+ with rf voltage at different sensitivity, and no filter in preamplifier was used.

The data in Figure 3-25 was normalized, as shown in Figure 3-26. In theory, the signal is supposed to reach a maximum at rf of 0 V because there should be no filtering at these amplitudes. Then signal should start to drop from apex with increasing rf voltage. However, our signals all increase first then decrease. The reason is that the rf voltage should drop to 0 volt

from $8.3 V_{pp}$ rapidly at the end of previous rf modulation cycle. But in our circuit, it takes some time to come back down to 0 Volt from $8.3 V_{pp}$. This causes the rising curve during 0-1 V_{pp} . Strictly speaking, that zero on x-axis is time 0 of one modulation cycle instead of voltage zero. The voltage at time zero is still $8.3 V_{pp}$. The rf voltage cannot drop to 0 from $8.3 V_{pp}$ instantaneously. It was also noticed that signal at 50 nA/V and 100 nA/V has a similar rising slope during 0-1 V_{pp} . The remaining sensitivity setting shares a different rising slope. The lower sensitivity, such as 200 nA/V and 500 nA/V, shows significantly shorter rise time. The higher sensitivity shows longer rising curve at the beginning of rf voltage. The problem may come from certain electronic unit inside preamplifier such as capacitor charging and discharging effect. Combining Figure 3-25 and Figure 3-26, 200 nA/V was chosen as sensitivity of preamplifier because it can both amplify properly and demonstrate accurate waveform.

Figure 3-26 Normalized argon signal variation with rf voltage at different sensitivity

3.4.4 Effects of Modulation Frequency on Signals

The effect of modulation frequency on signals was also investigated. The modulation frequency is easily adjusted on AFG. The time scale (sampling frequency) on the oscilloscope needs to match the applied modulation frequency to record a complete sampling cycle. For example we use modulation frequencies of 5 Hz, 250 Hz and 500 Hz on AFG. The horizontal scales on the oscilloscope are therefore 20 ms, 0.4 ms and 0.2 ms respectively. The sampling rates on oscilloscope are 50 KS/s, 2500 KS/s and 5000 KS/s respectively. Examples are shown in

Figure 3-27. The glow discharge voltage was -532 V at cathode, 105 V at anode with current 0.501 mA. The sampling gas was argon at 0.8 Torr. The rf frequency was 66 MHz. The preamplifier was set to 200 nA/V with no filtering. The results in Figure 3-27 show that lower modulation frequency has a sharp rising edge. The internal circuit of function generator and preamplifier has a fall time that is readily observable when the modulation frequency is faster but not observable with slow modulation frequencies like 5 Hz.

Figure 3-27 Argon signal comparison at different rf modulation frequency

3.4.5 Comparison of Oxygen and Argon Signal

Oxygen and argon were compared at the same amplification sensitivity and similar final measured currents. The pressure for oxygen and argon was 0.77 Torr and 0.60 Torr respectively. The rf input voltage was ramped from 0 to 120 mV_{pp} at 75 MHz which resulted in an applied waveform of approximately 0- 8.0 V_{pp} on the mass filter. After the raw signals were captured, they were processed using boxcar averaging method developed in matlab (see details in Appendix IV). Every adjacent twenty-five data point was averaged to one data point. 10 K data points were reduced to 400 points. The second derivative of the box-car averaged data is shown in Figure 3-28.

The second derivative shows two major peaks for argon and oxygen respectively. This is promising because they are probably oxygen m/z 32 and m/z 40. Unfortunately, the tuning circuit only worked well for a few days and we could not reproduce these results. We cannot tell the m/z that peak correspond to, either. But we can still verify whether the experimental peak ratio agree with calculated cut off voltage ratio because time is linear with cut off voltage and mass charge ratio according to Eiber's equation. The time ratio of oxygen and argon peak is 0.819 that is very similar to their mass to charge ratio 0.8. This result is therefore very promising.

Figure 3-28 The second derivative of transmitted ion signal from oxygen and argon plasmas at ~0.7 Torr. Loeb-Eiber filter operated at 75 MHz with frequency modulated ramp from 0 to 8 Vpp at 5 Hz.

The second-generation mass filter was broken due to frequent testing of rf tuning circuit. Figure 3-29 shows the broken second-generation mass filter. The connection socket 1 connects to a metal bar by a piece of conductive wire. The metal bar inside the mass filter connects every other mass filter wire. One problem is that the conductive wire does not contact the metal bar very well and frequently shorts. The second problem is that the connection socket 2 disconnects with metal bar because of the frequent testing of different transformers. We cannot fix this problem in our lab. We therefore need to send it back to Precision MicroFab for repair.

Connection socket 1

Connection socket 2

Figure 3-29 The broken second-generation mass filter

CHAPTER 4: DEVELOPMENT OF THE THIRD GENERATION, CHIP-BASED, LOEB-EIBER MASS FILTER

4.1 Construction of the Third-Generation Mass Filter

The third generation mass filter is a microfabricated $11\text{ mm} \times 11\text{ mm} \times 0.5\text{ mm}$ chip. The mass filter electrodes have a square cross section with dimension $25 \times 25\text{ }\mu\text{m}$ and space of $8\text{ }\mu\text{m}$, as shown from Figure 4-1 to Figure 4-3. The benefit of a chip-based mass filter is that the cost will be a lot lower in the long run. In addition, microfabrication can provide better tolerances and smaller errors. Moreover, our simulations have shown that square wires are slightly better than round wires because the ions undergo more oscillation cycles between the wires for a given applied rf waveform. The entire chip was microfabricated using relatively standard microfabrication techniques, as described later.

Figure 4-1 Photograph of the third generation Loeb-Eiber mass filter

Figure 4-2 The third generation Loeb-Eiber mass filter using square “wires” with a cross section of $25 \times 25 \mu\text{m}$, space of $8 \mu\text{m}$. The inset shows that the wires are electrically isolated at the ends. Image courtesy of Guido F. Verbeck, University of North Texas.

Figure 4-3 SEM image of one “wire”(e.g. green electrode in Figure 4-2)

The third generation mass filter is made using microelectromechanical system (MEMS) that use Silicon-on-Insulator (SOI) wafer as starting substrate. In our fabrication process - conducted by a subcontractor MUMPs (Multi-User MEMS), the first stage is to deposit phosphosilicate glass layer on top of a SOI wafer, as shown in Figure 4-4. And then annealed at 1050 °C in argon. The glass layer is then removed by wet chemical etching to leave phosphorous doped silicon. The second stage is to deposit a layer of negative photoresist on top of the SOI wafer. UV light is then exposed onto the negative photoresist through a

padmetal mask.

Afterwards, the photoresist is processed with a developing solution. Later, a metal stack is deposited onto the SOI and the photoresist is removed to form electrodes, as shown in Figure 4-5. We use this step to form the gold contact stripes by which we make electrical contact with the electrodes. The third stage is to cover a layer of positive photoresist that is UV-sensitive onto the SOI. The photoresist is then exposed to UV light through the SOI mask and subsequently treated with developing solution to remove the photoresist. The exposed silicon is processed by deep reactive ion etching with the result shown in Figure 4-6.

The fourth stage is to generate the structure of the bottom side, as shown in Figure 4-7. First, the front side protective material is applied on top of the SOI. Then the bottom side is coated with photoresist and patterned with a TRENCH mask layer. Afterwards, the bottom oxide layer is removed with reactive ion etching (RIE). The substrate is subsequently removed by deep reactive ion etching (DRIE). The middle oxide layer is processed by wet chemistry etch. The fifth stage is to remove both frontside protective material and the remaining oxide layer as shown in Figure 4-8. The protective material is stripped by dry etch process. The remaining oxide layer is handled with a vapor HF process.

Silicon		Substrate		Bottom Oxide		Shadow Mask
Oxide		Metal		PSG (dopant)		Frontside Protection Material

Figure 4-4 First step of microfabrication showing the deposition layer of phosphorsilicate (PSG) on a SOI wafer. Figure reproduced with permission from reference 64.

Figure 4-5 Electrode is deposited on top of SOI wafer through e-beam evaporation.⁷⁰ Figure reproduced with permission from reference 64.

Figure 4-6 The structure of silicon was formed through deep reactive ion etching (DRIE).⁷⁰ Figure reproduced with permission from reference 64.

Figure 4-7 Bottom side oxide and substrate layer are patterned then removed.⁷⁰ Figure reproduced with permission from reference 64.

Figure 4-8 Front protective material and the remaining oxide layer are removed.⁷⁰ Figure reproduced with permission from reference 64.

The process above is a general procedure. To fabricate the part, we first designed the different layers in Auto CAD. A screen capture of the 3rd generation Loeb-Eiber device in Auto

CAD is shown in Figure 4-2. We designed the device this way for two main reasons. Firstly, The device only has two electrodes, so it enables us to easily apply potentials to thousands of wires through only two electrical contacts. Secondly, each wire is supported by an insulating substrate at each end to provide structural integrity and prevent cantilevering. The third generation mass filter consists of two-piece interweaved grids as shown in blue and green color. Compared to the second-generation mass filter, it has smaller space, 8 μm vs 25 μm of previous design. This requires smaller voltage on adjacent electrodes to reach the same electric field strength. Moreover, the electrode is smaller too, 25 μm compared to 75 μm in previous design. The ratio of gap to electrode in current design is 0.32. The ratio of gap to electrode for the second-generation mass filter was 0.33. It means ion transmission ratio does not change very much. Figure 4-3 shows the supporting non-conductive substrate on the underneath side of the SOI chip to prevent the wires from cantilevering.

Since the gap between adjacent wires is very small, we have to be concerned with breaking down the air in between wires and the substrate-silicon dioxide. The dielectric strength of air and silicon dioxide are 3×10^6 V/m and 1×10^5 V/m respectively.⁷¹ The breakdown voltage in air assumes that the electrodes are far enough apart (>1 cm) to enable sufficient collisions between gas phase particles. The geometry of our device, with interelectrode gap of 8 μm does not fulfill this criterion. Because there are so few gas molecules between the gap at ~ 1 Torr, our

device cannot support a plasma, so does not follow the normal breakdown potential behavior.

Thus the dielectric strength of silicon dioxide is used to calculate the breakdown voltage.

For 8 μm distance, the breakdown voltage is expected to be $\sim 25 V_{pp}$. The practical breakdown voltage may be smaller than that because the material might contain defects, so the real dielectric strength might be smaller than the intrinsic dielectric strength.

4.2 Tuning Circuit

The capacitance of the third-generation mass filter was measured as 205 pF using a capacitance meter. After the BNC cable was connected, the capacitance was measured as 276 pF due to additional capacitance from coaxial cable. A tuning circuit was developed, as shown in Figure 4-9, to match this capacitance load. The tuning circuit consists of a transformer used to convert the primary rf from the AFG to two equal amplitude waveforms with phase angles that are 180 degrees out of phase, as described in section 3.3.3.3. This transformer uses an iron powder toroid core (T50-17 from Amidon). The test result is shown in Figure 4-10. The input is 5.0 V_{pp} at 40 MHz. The output is 2.0 V_{pp} .

Figure 4-9 Photograph of a center tapped tuning circuit for the third generation mass filter.

Figure 4-10 Test results of the tuning circuit from Figure 4-9, showing the desired equal amplitude and $\sim 180^\circ$ phase shift between the two outputs.

4.3 The Third Generation Mass Filter with EI Source

Initially, the third-generation mass filter was tested to provide principle demonstration at vacuum conditions ($<10^{-3}$ Torr) because it is relatively easy to generate, focus and detect ions at low

pressure. Ultimately, operation at pressures around 1 Torr is expected to be superior because ions will be collisionally cooled and have smaller velocities. The ions will therefore be more likely to undergo a maximum in oscillatory amplitude between the electrodes and be effectively filtered. The mass filter assembly includes EI source, lens stack and mass filter, as shown in Figure 4-11.

Figure 4-11 Photograph of the third-generation mass filter with ion optics system. A schematic of this system is provided in Figure 4-12.

This assembly was simulated in SIMION™ to optimize ions' behavior before testing, as shown in Figure 4-12. The simulations indicated the electrons (in red) emitted by the filament should not make it pass lens (4). In practice, using the voltages optimized in SIMION™ resulted in an excess of negative charge at the Faraday detector (11). Using 1 M Ω termination to the oscilloscope to monitor the ion current at detector (11) gave net negative ion (electrons) flux regardless of electrode settings. This may be because EI filament is in line with lenses, mass filter and detector. Thus we decided to modify this structure and build an orthogonal EI source.

Figure 4-12 SIMION simulation to show: A) equipotential contour in the lens stack, B) the potential field in lens stack, C) ions (black) and electrons' (red) flight path at 4 V_{pp} dipolar mode on the Loeb-Eiber filter, D) ions (black) and electrons' (red) flight path at 20 V_{pp} dipolar mode on the Loeb-Eiber filter. $V_1=V_2=-60$ V, $V_3=10$ V, $V_4=V_6=V_7=V_9=V_{10}=0$ V, $V_5=9$ V, $V_{11}=-1800$ V.

When we built this orthogonol EI source, we considered buying a commercial EI source. However, all the commercial EI sources were not readily compatible with our instrument configuration. We therefore built an EI source from scratch. Figure 4-13 shows a chip-based mass filter with an orthogonol EI source (Engineering schematics attached in Appendix V). The EI filament cover, repeller and electron sink were fixed on an insulated holder made of PEEK. The EI filament cover was designed with folded edges to prevent electrons moving into lens stack space. An electron sink was used to measure intensity of electrons transmitting through the ion source. The filament emits electrons that are accelerated to 70 eV to ionize the sample gas in the ion volume. The ions are repelled by ion repeller plate, focused by an Einzel lens stack before passing through the chip-based mass filter to the multiplier tube or Faraday collector.

Figure 4-13 Schematic to show chip-based mass filter with an orthogonal EI source. (The device has also been tested with a glow discharge ion source.)

After several weeks of experiments, we discovered an inherent problem with the mass filter holder. Originally, two grooves were carved on the mass filter holder. Two pieces of wire #40 AWG were glued into the groove. The tip of the conductive wire was bent to touch the gold ribbon on top of mass filter, so the contact force was dependant on the tensile strength of the #40 AWG copper wire. Because the wire was prone to moving during assembly, the device would frequently not show good electrical contact.

We modified the old configuration and used fine gold ribbons to make electrical connection to the gold conact stripes. The mass filter cover and container were both modified. The new design is shown in Figure 4-14. We applied a fine gold ribbon (0.135 mm $\times$ 0.0508 mm) to connect to gold contact strips. Standard push-pin connectors are used to connect the gold wires to a tuning circuit. This design has proved to be a dependable and reproducible method. This design also makes it easy to assemble and disassemble mass filter chips without damaging or scratching the chips.

Figure 4-14 Schematic and photograph to show mass filter support and connector

4.3.1 *Experimental Results under Vacuum with EI Source*

4.3.2 *Constructing EI Circuit*

The original idea to build the EI circuit is to copy an optimized design from commercial instrument. But it is very difficult to understand the electrical circuits of commercial instruments because they do not provide schematics. We therefore built the EI circuit by ourselves. The first thing is to know the electrical parameters. It is known that EI emits electrons with 70 eV. Also the filament has very low resistance, less than 1 Ω . The filament needs around 1 A of current, depending on the filament wire. We used a variety of wire material and gauges before settling on the most robust filament that was #40 gauge tungsten. If we build a voltage divider circuit, a relatively bulky ceramic resistor is needed. Thus, we came up with the following circuit, as

shown in Figure 4-15. A power supply 1 (TENMA 72-7295) provides current limited supply to heat the filament. A second power supply (TENMA 72-6909) provides an offset voltage to the filament for emitting energetic electrons. Power supply 1 should be able to provide current up to 2 A. The requirements for power supply 2 are not harsh, and it should be able to tolerate large current oscillation, up to 20 mA.

Figure 4-15 EI source electrical circuit.

The filament was first soldered on the holder. Then it was found that it easily came off the holder when filament was heated. It was probably that the temperature was so high as to melt the solder. Then we tried to spot weld the filament onto the holder. Spot welding was proved very robust and reliable. Different materials such as rhenium and tungsten are often used as EI filament material. Rhenium with diameter of 0.076 mm (W91 from Scientific Instrument Services) was tested in our instrument. The stability of our EI source was tested for 7 sccm N₂ at 8×10^{-4} Torr, as shown in Figure 4-16.. The current goes up from 1.253 Amps to 1.266 Amps in the first five minutes. The filament starts to get hot and is not stable in the beginning. Five minutes later, the filament become relatively stable. It was noticed that there is still small current oscillation; it is probably environmental temperature fluctuation cause this situation. Most commercial EI source has a heater that can keep the current stable. But ours doesn't.

The ion intensity was also tested through mass filter electrodes that were connected directly to an oscilloscope with 1 M Ω coupling. A positive signal about 10 mV was measured on the mass filter electrodes with 5 sccm Ar flowing into EI volume. This corresponds to 1×10^{-9} A. Given the dimension of mass filter, the mass filter has the maximum transmission efficiency 25%. This indicates there are approximately 2.5×10^{10} unfiltered ions before mass filter.

Figure 4-16 Plot to show the stability of home made EI source

The voltage-current characteristic is also measured, as shown in Figure 4-17. The resistance is in the range of 1.0 to 1.2 ohms. The filament gets hot when current goes through it. This causes resistance to increase. The slope increases with current, as shown in Figure 4-17. The operating current of EI filament has to be in a proper range. If it is too high, the life of filament is short. If it is too low, emission efficiency of electrons is too low. The proper current range should be from 1.2 to 2.5 Amps that correspond to 0.75 to 2.5 Volts.

Figure 4-17 Voltage-current characteristics of EI rhenium filament

4.3.3 *dc Voltage Optimization*

SIMIONTM software was used to optimize electric field parameters to maximize the ion current arriving at the detector. Figure 4-18 shows the flight path of argon and neon ions in simulated electrostatic fields. The voltage on the front ring and repeller are set at 9 V. Lens 1, Lens 3 and the end plate are all grounded. The voltage on lens 2 is set at -110 V. Through the simulations, we can understand how electrical parameters on each lens have effect on ions'

flight. We can use this simulation parameters as starting points to further optimize the actual operating parameters.

Figure 4-18 SIMION™ simulation to show argon ions (blue) and neon ions (green) in the new orthorgonal beam EI source. Electrons enter the ion source region orthorgonal to the page

In practice, we have two steps to optimize electrical parameters. The structure of instrument is shown in Figure 4-19. Firstly, we set the front ring, repeller, and three lenses at

zero Volt and optimized the voltage on the EI filament, EI cover and EI receiver in order to avoid negative signal on the mass filter. The signal on the mass filter was monitored by reading of the current via 1 M Ω terminated lead to the mass filter. The second step is to tune other parameters to get the largest positive signal on mass filter and the largest negative signal on electron multiplier. The final optimized voltage setup is shown in Table 4-1.

Figure 4-19 Schematic to show the configuration of a tested version of the orthogonal EI-Loeb-Eiber mass filter with electron multiplier detection.

Table 4-1 The electrical parameters of instrument

EI	2.56 V, 1.122 A
EI voltage	-25.5 V
EI cover	-50 V
EI receiver	0 V
Repelling plate	9.9 V
Front ring	46.7 V
Lens1	0 V
Lens2	-100 V
Lens3	0 V
End plate	0 V
Detector	-1600 V

4.3.4 Experimental Results for Argon and Neon

Before testing the mass filter with rf potentials, dipolar dc potentials were applied to the mass filter electrodes (e.g. +1 V to even-numbered electrodes, -1 V to the odd-numbered electrodes) to test the ability of the mass filter to block ions. Figure 4-20 shows that 1) all the neon and argon ions can be blocked with $<5 V_{pp}$ (dc), and 2) argon ions transmitted at slightly larger potentials ($4 V_{pp}$ vs $3.8 V_{pp}$) than neon under the same conditions, as expected.

Figure 4-20 Experimental multiplier responses at 5 sccm neon or argon respectively when the mass filter was operated in dipolar dc mode (e.g. + 2 V on even-numbered electrodes, - 2 V on odd-numbered electrodes).

The filter was then tested in dipolar rf mode. The results are presented in Figure 4-21. The filter was operated with a 40 MHz sine wave with a linear amplitude modulation from 0-7 V_{pp} at a rate of 5 Hz. Traces were averaged 512 times on the digital oscilloscope before exporting. The EI source and mass filter were at $\sim 8 \times 10^{-4}$ Torr Ar. The original signal contained high frequency noise, so it is necessary to manipulate or smooth the data to better understand the results. We therefore developed code in MATLAB to manipulate the data. Examples of a low pass FFT filter and derivative are provided in 1.1.1.1 Appendix IV. Firstly, data was smoothed with a low pass

filter of 1667 Hz to remove high frequency noise. Then the first and second derivative are applied on the filtered data to provide peaks at the inflection points, as shown in Figure 4-22 and Figure 4-23. Although the second derivative plot show some very promising looking peaks between 0.1 and 0.7 V_{pp} , indicating inflection points in the raw data, the peak at 0.5 V_{pp} corresponds to an ion of $m/z \sim 10$. The peaks at lower filter amplitudes correspond to m/z values less than 10, so are not the expected to be analytical signal.

Figure 4-21 Raw data collected from the 3rd generation chip-based Loeb-Eiber mass filter at $\sim 8 \times 10^{-4}$ Torr.

Figure 4-22 First derivative of the experimental data from the 3rd generation Loeb-Eiber mass filter shown in Figure 4-21.

Figure 4-23 Second derivative of the experimental data from the 3rd generation Loeb-Eiber mass filter shown in Figure 4-21.

The argon ion signal with different flow rates/number densities are compared in the EI source, as shown from Figure 4-25 to Figure 4-26. The filter voltage position of the peaks (at filter amplitudes less than 0.7 V_{pp}) are extremely sensitive to experimental conditions, which was not expected. A small change in pressure or ion signal should not shift the filter amplitude position of a peak, but could/should influence the slope of the raw signal before and after the inflection point. No obvious comparisons are present between the different flow rates from the second derivative plot. The flow significantly affects the position of the inflection points at these low pressures. We came to understand that the problem probably stems from operating the mass

filter at pressures less than 0.1 Torr. Under vacuum conditions, the KE of ions will have very significant effect on mass filtering because the assumption that ions undergo a sufficient number of collisions is not valid. We actually need relatively high-pressure conditions ($\sim$ Torr) to provide collisional dampening to the ions to slow them down.

Figure 4-24 The original experimental data from the 3rd generation Loeb-Eiber mass filter at different flow rates.

Figure 4-25 First derivative of the experimental data from the 3rd generation Loeb-Eiber mass filter at different flow rates

Figure 4-26 Second derivative of the experimental data from the 3rd generation Loeb-Eiber mass filter at different flow rates of argon.

4.4 Experimental Results under High Pressure with Glow Discharge

4.4.1 *dc and rf Voltage Optimization*

We used a similar lens stack as in Chapter 3.4.1 because they both work at relatively high pressure (around 1 Torr), the dc voltage used is also similar with that, as shown in Figure 3-21.

The rf output was controlled using AFG (AFG 3252, Tektronix) and the rf amplifier (525 LA, Electronic Navigation Industries), through a custom tuning circuit to the mass filter. The rf amplifier has a 50 dB nominal gain with ± 1.5 dB variation. The measured rf voltage at 49.8 MHz is shown in Table 4-2. Cont CH means the potential V_{pp} of one side of mass filter relative to

ground at continuous sinusoid waveform. Modu CH1 represents the voltage amplitude V_{pp} of one side of mass filter relative to ground at modulated sinusoid waveform with modulation frequency 50 Hz.

Table 4-2 rf input and output at continuous and modulation mode

AFG 3252 (mV)	Cont CH1 (V)	Cont CH2 (V)	Modu CH1(V)	Modu CH2 (V)
50	1.54	1.48	1.43	1.39
60	1.81	1.78	1.72	1.67
70	2.11	2.09	2.02	1.97
80	2.44	2.38	2.31	2.28
90	2.74	2.67	2.62	2.59
100	3.04	2.99	2.94	2.88
110	3.38	3.29	3.12	2.92
120	3.68	3.59	3.34	3.30
130	3.99	3.90	3.54	3.64
140	4.31	4.20	3.90	3.82
150	4.65	4.51	4.22	4.20
160	5.03	4.82	4.46	4.28
170	5.30	5.20	4.76	4.60
180	5.64	5.55	4.96	4.88
190	5.96	5.91	5.20	5.04

4.4.2 *Effects of Pressure on Results*

Argon was used as the sample to test the performance of the mass filter at different pressures, as shown in Figure 4-27. The glow discharge was set with cathode at -346 V and current 0.551 mA. The rf input was 100 mV_{pp} with a 47.2 MHz sine wave with a linear amplitude modulation at a rate of 50 Hz. Current preamplifier is set with sensitivity of 100 nA/V. Traces were averaged 512 times with 20 MHz low pass filter on the digital oscilloscope before exporting. From the results, the transmitted ion signal gets lower with increasing pressure, which agrees with what we expect because fewer ions can arrive at detector at higher pressure. We also notice that it becomes easier for ions to get filtered at higher pressure. After we normalized the data, the filtering effects become more obvious, as shown in Figure 4-28. At 2.69 Torr and 2.43 Torr, the ions' curve start to become flat at close to 3 V_{pp} which indicates all ions are filtered. The ions continue to go down at close to 3 volt V_{pp} for other pressures.

Figure 4-27 Raw data of argon at different pressure

Figure 4-28 Normalized detector response of oxygen ions in positive mode as a function of rf amplitude

We also did a principle demonstration about rf voltage. Figure 4-29 shows detector response with different rf voltage amplitude. The same time axis represents different rf voltage scales. At higher rf voltages, more ions can be filtered, which agrees with what we expect.

Figure 4-29 Detector response variation with different rf voltage amplitudes. The rf amplitude is linearly ramped from 0 V to 8 V over the 20 ms period

Argon and oxygen are compared at the same gain 100nA/V. In theory, the oxygen and argon should have inflection points at 0.47 (O^+), 1.17 (Ar^+) V_{pp} respectively. The result shows that they have similar inflection points at around 1.8 V_{pp} . One possible reason is that data are captured at different pressure in order to get the similar unfiltered signal or similar intensity of signal. But the pressure should not change the position of inflection point. Another concern about our data is that the voltage is measured on the connection socket outside mass filter. Each

connection socket is connected with mass filter through a piece of gold ribbon about 0.4 inches long. Thus the voltage we measured may not reflect the real voltage on the mass filter. In addition, the voltage we measured on mass filter is also not symmetrical, as shown in Table 4-2. At the end of rf modulation cycle, from 3.0 to 4.0 Volt, the signal curve starts to move up because of voltage imbalance.

Figure 4-30 Comparison of oxygen and argon signals in positive ion mode at 47.2 MHz

4.5 Problems with the Third-Generation Mass Filter

During our experiments with the third generation mass filter, some drawbacks were found. First, the conductive ribbon on the mass filter is very small (0.135×0.0508 mm), and therefore very difficult to measure the resistance and capacitance. During measurement, the probe of voltmeter caused scratches on the gold contact stripe, as shown in Figure 4-31. Sometimes the distributed gold would short the two electrodes on the chip. Secondly, the mass filter stay in the air at atmosphere pressure for a long time since we need to spend lots of time developing and testing our tuning circuit. The dust in air may get to the mass filter, as shown in Figure 4-32. The white dots are dust. This may also cause shorting or charging problems. Thirdly, the third generation has capacitance around 206 pF. It is difficult to make resonance circuit at expected frequency like 68 MHz because the parasitic inductance on the conductive wire may exceed the required resonance inductance at high frequency. Thus, no matter how small the inductance of our second coil is, it is too hard to create a resonant circuit at 68 MHz.

Figure 4-31 Scratched gold ribbon on the third generation mass filter under microscope

Figure 4-32 Dust on the third generation mass filter under the microscope

4.6 Construction of the Fourth Generation Mass Filter

They are always optimized during experiment and usage. Considering the drawback of the third generation mass filter, Dr. Hoffmann in our group developed the fourth generation mass filter. He increases the width of conductive gold ribbon to 2.31 mm from 0.05 mm that makes measurement much easier. The effective transmission area was reduced in order to decrease the capacitance. Four categories of mass filters with different dimensions are designed. The first type has effective transmission area $4\text{ mm} \times 4\text{ mm}$. The wire is $10\text{ }\mu\text{m}$ in width with adjacent gap $10\text{ }\mu\text{m}$. The second type has effective transmission area $4\text{ mm} \times 4\text{ mm}$. The wire is $20\text{ }\mu\text{m}$ in width with adjacent gap $10\text{ }\mu\text{m}$, as shown in Figure 4-33. The third type has effective transmission area $4\text{ mm} \times 4\text{ mm}$. The wire is $40\text{ }\mu\text{m}$ in width with adjacent gap $10\text{ }\mu\text{m}$. The fourth type has effective transmission area $2\text{ mm} \times 2\text{ mm}$. The wire is $20\text{ }\mu\text{m}$ in width with adjacent gap $10\text{ }\mu\text{m}$. The capacitance for each dimension is listed in Table 4-3.

Table 4-3 The capacitance for the fourth generation Loeb-Eiber mass filter

Dimension (wire)×(space)×(hole)	Capacitance
10μm ×10μm ×4 mm	255 pF
20μm ×10μm ×4 mm	259 pF
40μm ×10μm ×4 mm	254 pF
20μm ×10μm ×2 mm	282 pF

Figure 4-33 Comparison of the third and fourth generation mass filters, the left one is the third generation mass filter, the fourth generation mass filter is on the right.

4.7 Expected PCB Circuit with Mass Filter

During the development of the mass filter, I spent most time developing the tuning circuit. They do not seem perfect. Our next step is to integrate our fourth generation mass filter into the printed circuit board (PCB). The transformer can be drawn on the board that can reduce parasitic capacitance and inductance. Our mass filter can be connected via wirebonding. But this is not convenient to assemble and disassemble the mass filter. Once the mass filter is broken, we have to make another wirebonding. Another alternative way is to use commercial mini circuit such as six-pin DIP circuit to couple with our chip mass filter.

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Appendix I Workbench User Program

User Programs

```
--      SIMION 8.0 equivalent of a SIMION 4.0 .ELE user program
--      Based on D.A. DAHL 1994. D. Manura-200608-Lua version.-
--      this fast_adjust segment creates a simple rf field between
--      the plates and round electrodes using dynamic fast adjust

SIMION.workbench_program()

adjustable omega = 100          -- frequency (MHz)

adjustable rf_voltage = 0.8     -- rf voltage

adjustable pe_update_each_usec = 0.3    -- PE display update time step (usec)

-- SIMION fast_adjust segment.  called to override electrode potentials.

function segment.fast_adjust()

    -- Set electrode voltages.

    adj_elect01 = rf_voltage*sin(ion_time_of_flight * frequency*6.283185307)

    adj_elect02 = - adj_elect01

end

-- SIMION other_action segment.  called on each time-step.

local next_pe_update = 0      -- next time to update PE surface display (usec)

function segment.other_actions()
```



```

--Note: the following is optional and is only for display purposes.

-- Trigger PE surface display updates.

-- If TOF reached next PE display update time...

if ion_time_of_flight >= next_pe_update then

    -- Request a PE surface display update.

    sim_update_pe_surface = 1

    -- Compute next PE display update time (usec).

    next_pe_update = ion_time_of_flight + pe_update_each_usec

end

end

function segment.tstep_adjust()

    -- For the trajectory calculation to be reliable, the time step size should

    -- be no more than some fraction of the rf period so that the ion sees each

    -- rf cycle as it exists.

    -- In the SIMION quadruople example under minimum trajectory quality (0)

    -- and default conditions, ion_time_step is already below one-tenth the

    -- rf period, so this code isn't really necessary. However, this code

    -- reduces the chance of surprises in case the conditions are changed

    -- and trajectory quality factor is set too low.

```

```

-- The performance overhead of this is quite low (~1%).

-- Keep time step size <= X usec.

ion_time_step = min(ion_time_step, 0.001) -- X usec

end

```

Appendix II Geometry Language Codes

```

pa_define(4000,4000,1,p,none,e)

locate(1000,1755)

{
e(1)

{
locate(20,0)

{fill{within{circle(0,0,125,125)}}}}

}

e(2)

{
locate(20,320)

{fill{within{circle(0,0,125,125)}}}}

}}

```

Appendix III Signal Acquisition Using Labview

Most commercial mass spectrometers acquire data with just a click on the computer. I also did a little exploration about this area. G programming inside Labview is very popular to make operator interface. It uses graphical code to define any function you want such as creating channel, generating data, acquiring data and processing data in block diagram. It generates a separate screen—front panel to provide knob to operate and graph to view data. It also requires PCI or PXI card to support software operation. We have two PCI cards---PCI 6733 and PCI 6229. The NI PCI 6733 is high-speed analog output cards and it has eight analog outputs with updating rates up to 1 MS/s per channel without analog input. It is able to generate a waveform up to 500 KHz. NI PCI 6229 is a multifunctional data acquisition card. It has thirty-two analog inputs at 16 bits, 250 kS/s and four analog outputs at 16 bits, 833 kS/s. Derrel had already used eight analog inputs of PCI 6229 and eight analog outputs of PCI 6733 to make voltage control interface with Labview SignalExpress⁷². I can still use analog inputs of PCI 6229 to acquire data.

The data acquisition block program is shown in the diagram below. First, a function-DAQmx creat channel was used to designate a channel of PCI 6229 to obtain data. Then the second function-DAQmx timing defines the number of samples, sampling rate and the source of sample clock. After that, data is sent to a while loop structure and captured continuously. Data are measured by a function-DAQmx Read inside the 2 data are graphed in the front panel. Then,

a butterworth filter is also used in our program to filter low or high frequency noise. Filtered signal is also presented in the front panel.

Figure A III-1 Schematic shows continuours data acquisition within Labview 7.1

Table A III-1 List and description of subprograms for Figure above

#	Program name	Description
1	DAQmx Create Channel.vi	Create channel(s) to measure voltage
2	DAQmx Timing.vi	Sets the source of the Sample Clock, the rate of the Sample Clock, and the number of samples to acquire or generate
3	DAQmx Start Task.vi	Transits the task to the running state to begin the measurement
4	DAQmx Read (Analog 1D DBL 1Chan NSamp).vi	Reads one or more floating-point samples from a task that contains a single analog input channel
5	Butterworth Filter.vi	Generates a digital Butterworth filter by calling the Butterworth Coefficients VI
6	Error Cluster From Error Code.vi	Converts an error or warning code to an error cluster
7	DAQmx Clear Task.vi	Clears the task
8	Simple Error Handler.vi	Indicates whether an error occurred

Figure A III-2 Graphical user interface for data acquisition

Appendix IV Matlab Code for Box-Car Average

The code below is the main program. It can do baseline correction, normalization, and derivatization. The green words are explanation for every line of code.

```
clear variables; %removes all variables from workspace
clc; % clear all input and output from the command window display
close all %deletes all figure windows whose handles are not hidden
set(gca, 'fontname', 'verdana');
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

```

r=25;
coeff=1; % the constant to convert time
axis to voltage axis
m = csvread('fj072413_4.csv',0,3,[0,3,9999,4]); % Read data from
.csv file
x = m(401:end,1);
%x2=m(:,1)*62.5;
y = m(401:end,2);
ymax=max(y);
ymin=min(y);
yproc=(y-ymin)/(ymax-ymin); % Baseline correction and
normalization for y axis
[x6,y6,z5,z6] = boxcar(x,yproc,r,coeff)
m = csvread('fj072413_2.csv',0,3); % Read data from .csv file
x4 = m(401:end,1);
%x2=m(:,1)*62.5;
y4 = m(401:end,2);
ymax2=max(y4);
ymin2=min(y4);
yproc2=(y4-ymin2)/(ymax2-ymin2); % Baseline correction and
normalization for y axis
[x7,y7,z7,z8] = boxcar(x4,yproc2,r,coeff)
plot(x*coeff,y,'blue')
hold on
plot(x4*coeff,y4,'g')
xlabel('Time');
ylabel('Intensity');
title('Comparison of original data for O2 and Ar');
hleg1=legend('O2','Ar ');
hold off
figure(gcf+1)
plot(coeff*x6(1:end-2),z6,'blue')
hleg=legend('O2')
hold on
plot(coeff*x7(1:end-2),z8,'g')
xlabel('Time (s)');
ylabel('2nd derivative of Intensity');
title('Comparing 2nd derivative of O2 and Ar');
hleg=legend('O2','Ar ');
hold off

```

The code below is function call. Its main function is to do box-car average.

```

function [x3,y3,z1,z2] = boxcar(x,y,r,coeff)
n = length(x);
len1 = n/r;

```



```

q = 1;
j=1;
for i = 1:r-1
    t = 1;
    for ii = len1*(q-1)+1:len1*q
        y2(t) = y(ii);
        x2(t) = x(ii);
        t=t+1;
        ii
    end

    y3(j)=mean(y2);
    x3(j)=median(x2);
    j=j+1;
    i
    q=q+1;
end

plot(x*coeff,y)
hold on
plot(x3*coeff,y3,'ro')
hleg2=legend('raw data','box car averaged data')
figure(gcf+1)
z1 = diff(y3)/0.000002;
z2 = diff(y3,2)/(0.000002*0.000002);
plot(coeff*x3(1:j-2),z1,'ro')
figure(gcf+1)
plot(coeff*x3(1:j-3),z2)
figure(gcf+1)

```

Appendix V Mechanical Drawings

Figure A V-1 Engineering schematic for BNC feedthrough adaptor

Figure A V-2 Engineering schematic of the container for the second-generation mass filter

Figure A V-3 Engineering schematic of the cover for the third-generation mass filter

1. Material: stainless steel
2. Amount: 1
3. Four holes with diamter of 0.125 fit over ceramic tube.
4. Two holes with diameter of 0.066 fit screw of 0.079 inch.
5. Unit: inch

Designed by: Glen Jackson, Feng Jin

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Figure A V-4 Engineering schematic of orthogonogonal EI filament support

Figure A V-5 Engineering schematic of peek block for supporting ion repeller plate

Figure A V-6 Engineering schematic for the first lens

Figure A V-7 Engineering schematic for EI filament holder

Figure A V-8 Electron sink used to collect electrons from EI filament

Figure A V-9 Engineering schematic for EI filament cover

Resume

Education

West Virginia University (WVU), Morgantown, WV

- ◆ Ph.D. in Analytical Chemistry expected in December, 2014 with Dr. Glen P. Jackson

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- ◆ Ph.D. Candidate in Analytical Chemistry, with Dr. Glen P. Jackson

Dalian Institute of Chemical Physics, Chinese Academy of Sciences (DICP), Dalian, China

- ◆ M.S. in Analytical Chemistry

Zhengzhou University (ZZU), Zhengzhou, China

- ◆ B.S. in Polymer Materials and Engineering

Research and Teaching

Development of a Portable Loeb-Eiber Mass Spectrometer for Operation at 1 Torr

- ◆ Simulated ions' trajectories using SIMION to optimize geometry and electric potentials of the mass filter system
- ◆ Built an operator interface in LabVIEW to control the mass spectrometer
- ◆ Designed and built different EI source and glow discharge ion sources
- ◆ Designed, built and tested rf tuning circuits and transformers in the range of 1-80 MHz
- ◆ Processed data in Matlab and Origin using different algorithms and smoothing methods

Development of a Portable Orthogonal Time of Flight Mass Spectrometer

- ◆ Made programs using Matlab and SIMION software to calculate and simulate ion flight trajectory
- ◆ Designed a vacuum ultraviolet ion source with a pulse extraction region and field free region using Solidworks
- ◆ Designed a detector circuit with micro channel plate
- ◆ Optimized electrical parameters of mass spectrometer

- ◆ Investigated chemical properties of nano-aerosol in smoke and vehicle emission
- ◆ Conducted real-time monitoring experiments of ambient volatile organic compounds

Teaching Assistant

- ◆ Teaching advanced analytical chemistry lab courses using various analytical methods such as AAS, ICP-OES, FTIR, Raman, UV-Vis, Fluorescence and GC/MS

Awards

- ◆ 2nd place Award in Ohio University Research Expo
- ◆ Excellent undergraduate thesis award at ZZU
- ◆ 4 Merit-based Scholarship for each undergraduate academic year in ZZU
- ◆ National 2nd class scholarship

Presentations

- ◆ Jackson, G.P., Jin, F., Hoffmann, W.D., “On the Theory and Design of a Loeb-Eiber Mass Filter”, in prepration.
- ◆ **Jin, F.**; Hoffmann, W.D.; Verbeck, G.F.; Jackson, G.P., “Development of a Portable Mass Spectrometer for Operation at 1 Torr”, 61th ASMS Conference on Mass Spectrometry and Allied Topics, Minneapolis, MN, June 2013
- ◆ **Jin, F.**; Verbeck, G.F.; Jackson, G.P., “Development of a Portable Mass Spectrometer for Operation at 1 Torr”, 59th ASMS Conference on Mass Spectrometry and Allied Topics, Denver, CO, June 2011

References

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