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THE DEVELOPMENT OF NEW QUADRUPOLAR MASS SPECTROMETRIC
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by

Ronald Edward Reinsfelder

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF CHEMISTRY
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

1977
I hereby recommend that this dissertation prepared under my direction by Ronald Edward Reinsfelder entitled The Development of New Quadrupolar Mass Spectrometric Techniques and Their Application to Chemical Analysis be accepted as fulfilling the dissertation requirement for the degree of Doctor of Philosophy.

Dissertation Director

As members of the Final Examination Committee, we certify that we have read this dissertation and agree that it may be presented for final defense.

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SIGNED: Ronald E. Reinsfelder
To Suzie --

for the patience, the understanding, and the love.
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ABSTRACT

The concept of Separator Analyzer Mass Spectrometry (SAMS) is experimentally evaluated. Attention is focused on the use of the quadrupole as a notch filter for the rejection of single mass ions or bands of ions of multiple masses. This mode of operation, which can tolerate ion currents a million times greater than the mass filter, offers a viable approach for the analysis of trace level species diluted in great volumes of host matrix. A discussion of both the formal and qualitative theories is given.

The basis for notch filter ion rejection involves the application of energy at some fundamental frequency of ion motion in addition to the strong focusing quadrupole field. The supplementary field may be either quadrupolar or homogeneous in nature. Energy is absorbed by the resonant ion and causes an increase in the amplitude of ion trajectory. If the time spent by the ion in the supplementary field is sufficient (usually one resonance field cycle), then resonant ions obtain amplitudes larger than the instrument field radius, strike the electrodes, and are discharged as neutrals. The rejection notch width in atomic mass units (AMU) increases with increasing resonance field voltage. Ions heavier and lighter than the resonant ion oscillate in the beat frequency and are also discharged if their trajectory amplitudes exceed the quadrupole field radius.
The SAMS system described here employs two tandem quadrupoles mounted between the ion source and the detector. The second quadrupole is operated as a conventional mass filter, while the first is utilized as a notch filter. The notch filter, or separator, rejects unwanted ions while passing those of interest on to the mass filter for mass spectrometric analysis. The system is, by its nature, suitable for direct atmospheric analysis and should prove to be a versatile detector for gas and liquid chromatographs.

Considerations involved in the design and construction of such systems are discussed and the construction of a simple inexpensive quadrupole filter assembly is detailed. Mechanical and electronic tolerances and their relationship to filter performance are also presented. Experiments are described which assess the optimization of the notch filter quadrupole field. For maximum ion transmission, the dc component is kept at zero and only the radiofrequency ac potential is applied. All ions above a certain low mass cutoff are transmitted. This low mass cutoff is a function of the frequency and voltage of the applied notch filter quadrupole field and the field radius of the quadrupole filter.

Additional experiments are presented which evaluate the nature and efficiency of the resonance rejection of the notch filter. Rejection of more than 99.9% of the diatomic nitrogen and oxygen is obtained with no apparent loss of monatomic nitrogen and oxygen ions. A study relating the resonance field voltage and the mass width of the rejection
notch is reported. Suggestions for a differentially pumped analytical SAMS system are also presented.

The final chapter deals with a related project utilizing a commercial gas chromatograph-mass spectrometer-computer system. A computerized approach for the acquisition of stable isotope ratios of 0.1% relative standard deviation using peak area integration techniques is presented. Both pure and chromatographic samples with isotope ratios as high as 162 to 1 are considered.
CHAPTER 1

GENERAL INTRODUCTION

The analytical chemist today is presented more and more with problems involving the identification and quantitation of trace level species in a variety of diverse matrices. The analysis of trace metals has been accomplished using a variety of atomic spectrochemical techniques. Trace level organic species, especially those of biomedical interest, have remained somewhat more difficult to analyze. Although great advances in the area of chromatographic separations have occurred, most compound identifications are still assigned solely on the basis of column retention volume data. This practice requires the use of pure standards and presents, at best, uncertain results where adequate standards are either impractical or impossible to obtain. The ideal detector for organic samples should be able to identify components with no reliance on standard availability and should also be applicable to quantitation for sample concentrations of 1 part per million or less.

Mass spectrometry is ideally suited to meet these qualifications and has recently undergone a transformation that has established the mass spectrometer as a reliable and essential tool of the analytical chemist. A large part of this revitalization is due to the rapid commercial development of the quadrupole mass filter, often referred to by the misnomer, spectrometer, during the past decade, especially as a gas
chromatographic detector. Three major reasons can be cited to explain the rapid acceptance of the quadrupole as an analytical instrument.

First, the versatility of the quadrupole mass filter permits the operator to select any compromise between resolution and sensitivity suitable to a specific analysis by a simple electronic adjustment. No recourse to slit width changes or other hardware modifications are necessary. Secondly, in an age where digital computers provide the most viable approach for processing the quantities of data resulting, the ability to readily implement interfacing with a quadrupole cannot be over-emphasized. All necessary control functions can be accomplished easily using low voltage switching and the linear mass range is easily scanned by incrementally stepping the low voltage can ramp using standard digital-to-analog devices. Finally, the ability of the quadrupole to retain good performance characteristics while operating at pressures more than three orders of magnitude above those of conventional mass spectrometers has established its position as a valuable chromatographic detector.

The ability of the quadrupole mass filter to operate at elevated pressures is a direct consequence of its fundamental properties. It is a strong focusing analyzer which means that ion trajectories through the instrument are subject to constant correction. The ions of the magnetic and time-of-flight instruments are given an initial impulse, usually in the form of an accelerating voltage, and the ions are passively separated according to a mass related property. In magnetic analyzers the ions are sent through a uniform, stable magnetic field and spatially
separated according to their trajectories which have radii proportional to the respective momentum of each ionic species. In time-of-flight analyzers the ions are separated as a function of velocity during passage through a field free drift region and resolved as a function of the drift time which varies inversely with the square root of the ion mass. In either case, the maximum operating pressure is determined by the onset of ion-molecule collisions and ion-ion repulsions which degrade the performance.

The performance of the quadrupole analyzer is not solely dependent upon the initial impulse the ions receive prior to entering the analyzer. The dynamic, strong focusing nature of the electrostatic quadrupole field acts to correct ion trajectories which are deflected from stable paths by ion-molecule or ion-ion interactions. For this reason, the quadrupole is relatively insensitive to high pressure degradation effects. In fact, the upper pressure of a quadrupole mass spectrometer equipped with an electron impact ion source is normally limited by the ion source which ceases to efficiently function at a pressure two orders of magnitude lower than that at which the analyzer performance begins to degrade (Brubaker 1969, p. i).
CHAPTER 2

GENERAL THEORY OF THE QUADRUPOLE MASS FILTER

Historical Development

Previous to the development of the quadrupole, most commercial mass spectrometers operated by measuring two of the three ion properties of momentum, energy, or velocity. Mass separation was either spatial as for the magnetic sector instruments or temporal as for the time-of-flight analyzers. The first mass spectrometers were Thomson's (1913) parabola instrument and Aston's (1919) velocity focusing device. The magnetic mass spectrometer from which today's instruments derive their origins was developed during the early Thirties. Time-of-flight instruments were developed during the late Forties and early Fifties after the technique was initially proposed by Stephens (1946).

The use of an electrostatic quadrupole mass analyzer was first proposed by Paul and Steinwedel (1953) in Germany and by Post (1953) at the University of California Radiation Laboratory. Only Paul and Steinwedel's work appeared in the open literature. The concept of the electrostatic quadrupole can ultimately be traced back to 1952 when Courant, Livingston, and Snyder (1952) used strong focusing quadrupolar magnetic fields to compress proton beams first in one plane, then in a second plane perpendicular to the first. Blewett (1952) accomplished strong focusing using electrostatic quadrupole fields, and shortly
thereafter Paul and Steinwedel (1956) applied for a patent on the quadrupole mass filter.

In 1955, Paul and Raether (1955) showed that the electrostatic quadrupole could be operated in a manner which exhibited ion transmission characteristics similar to those of a conventional mass spectrometer. This was the origin of the quadrupole mass spectrometer so widely used today. In March 1960, W. M. Brubaker (Carignan, in Dawson 1976, p. 274) produced what is thought to be the first quadrupole mass spectrum in the United States. This event marks a significant transition in the history of quadrupole development. Just as Paul and his group had dominated the early quadrupole developments of the Fifties, so Brubaker was at the forefront of quadrupole research during the Sixties. Brubaker received support for this work from various government agencies interested in the quadrupole as an upper atmosphere, rocket-borne mass analyzer. It was, in fact, upper atmospheric work that supported quadrupole development until the surge of interest in gas chromatography-mass spectrometry (GC-MS) as an analytical tool led to the widespread application and development that typify quadrupole research today.

**Nature of the Applied Quadrupole Field**

The value of the potential at any point in the quadrupole field can be expressed as a function of its position. For Cartesian coordinates x, y, and z, the potential, E, is given by

\[ E = E_0 (\lambda x + \sigma y + \gamma z) \] (1)
where \( E_0 \) is a position-independent factor characteristic of the applied potential waveform. The terms \( \lambda, \sigma, \) and \( \gamma \) are weighting factors for the \( x, y, \) and \( z \) positional coordinates. Since each of the three dimensions can be considered separately, the applied field is uncoupled in each direction and the motion of a charged particle in any one direction is independent of its motion in the other two directions. This fact greatly simplifies the mathematical analysis of the quadrupole field.

Assuming there are no space charge effects within the field region bounded by the electrodes, Equation 1 must be governed by the limits imposed by Laplace's equation since the applied potential field is assumed to be quasi-static. Laplace's equation states that

\[
\nabla \cdot E = 0
\]

which, in turn, implies that

\[
\lambda + \sigma + \gamma = 0
\]

The simplest method of satisfying Equation 3 is also the solution applicable to the operation of the quadrupole mass filter:

\[
\lambda = -\sigma \quad \text{and} \quad \gamma = 0
\]

Having characterized the nature of the quadrupole field, it is now necessary to specify the exact form of the potentials to be applied to the electrodes. Consider the electrical potential at a point in the \( x \) direction, \( E_x \). Since
the form of the applied potential, $\phi$, can be found by integration. A suitable representation is

$$\phi = - \frac{1}{2} E_0 (\lambda x^2 + \sigma y^2 + \gamma z^2)$$

Taking into account the relationship indicated by Equation 4, the following statement of the applied potential is obtained:

$$\phi = - \frac{1}{2} E_0 \lambda (x^2 - y^2)$$

Equation 7 indicates that the equipotential lines present in the field region between the electrodes are sets of rectangular hyperbolae in the $xy$ plane possessing a fourfold symmetry about the $z$ axis. This conclusion is graphically depicted in Figure 1.

**Electrode Geometry**

The optimum electrode geometry used to produce the equipotential surfaces of Equation 7 and Figure 1 is shown in Figure 2. The structure consists of four mutually parallel hyperbolic electrodes positioned in a circular array so that each electrode is exactly $90^\circ$ from each of its neighboring electrodes. The linear distance between opposite electrodes is twice the field radius, $r_0$. Spatially opposing electrodes are electrically connected in pairs so that two sets of electrodes that can be arbitrarily termed $x$ and $y$ are formed.
Figure 1. Quadrupole field equipotential field surfaces.
Figure 2. Ideal hyperbolic quadrupole filter geometry.
The Form of the Applied Potential

For the quadrupole mass filter, the constants are selected so that

$$\lambda = - \sigma = - \frac{1}{r_o^2} \quad (8)$$

Equation 8, when substituted into Equation 7, yields the following relationship:

$$\phi = E_o \frac{(x^2 - y^2)}{2r_o^2} \quad (9)$$

It remains then to specify the form of the applied potential, $E_o$. If the potential between physically adjacent electrodes (i.e., $x$ electrode pair relative to $y$ electrode pair) is $\phi_o$, then the applied potential of Equation 9 becomes

$$\phi = \phi_o \frac{(x^2 - y^2)}{2r_o^2} \quad (10)$$

The form chosen for $\phi_o$ has conventionally been

$$\phi_o = (U - V \cos \omega t) \quad (11)$$

Therefore, $\phi_o$ consists of a time-independent or dc potential, $U$, and sinusoidal time-dependent ac potential, $V \cos \omega t$, where $t$ is the time
and ω is the angular frequency. The angular frequency can be related to the frequency of the applied voltage, f, by

$$\omega = 2\pi f$$  \hspace{1cm} (12)

**Ion Motion in a Quadrupole Field**

From Equation 10 it is obvious that for any point (x,y) within the field region a time-dependent potential exists which increases with the radial displacement of that point from the z axis (i.e., ground potential) of the mass filter. Therefore, the force, e\( \phi \) (where e is the charge of an electron), experienced by an ion traversing the quadrupole field increases as the ion is displaced further from the center of the field. This effect is referred to as strong focusing and is responsible for many of the advantages exhibited by the quadrupole mass filter.

The equation for ion motion in the x direction is obtained by equating the forces which act to repel and attract an ion of mass, m, traversing the field region:

$$m \left( \frac{d^2x}{dt^2} \right) = eE_x$$  \hspace{1cm} (13)

Rearrangement and substitution using Equations 1 and 8 yield the following relationship for the motion of an ion in the x direction:

$$\frac{d^2x}{dt^2} + \left( \frac{e}{mr_0^2} \right)(U - V \cos \omega t)x = 0$$  \hspace{1cm} (14)
Since the ion motion in the y direction is symmetrical and differs only by the sign of the weighting factor, the following relationship is obtained:

\[
\frac{d^2 y}{dt^2} - \left( \frac{e}{mr_o^2} \right) (U - V \cos \omega t)y = 0
\]  

(15)

Similar analysis of the z component of ion motion gives

\[
m(\frac{d^2 z}{dt^2}) = 0
\]  

(16)

which implies that ion motion down the length of the mass filter parallel to the electrodes is totally independent of any potential applied to the electrodes.

Since Equation 16 is trivial, only Equations 14 and 15 need be considered to totally describe the motion of an ion in a quadrupole field. Equations 14 and 15 belong to a class of equations known as the Hill equations. They can be fitted to the canonical form of a subclass of the Hill equations known as the Mathieu equations by making the following substitutions. Since the x and y equations are analogous except for a sign difference they will be treated using the more general variable, u, to represent either direction:

\[
a_u = a_x = -a_y = \frac{8eU}{m\omega^2 r_o^2}
\]  

(17)
The resultant Mathieu equation is

\[ \frac{d^2u}{d\xi^2} + (a_u - 2q_u \cos 2\xi)u = 0 \] (20)

The properties of the Mathieu equations are well-established in the literature (McLachlan 1951) and will be treated here only insofar as they pertain to the understanding of quadrupole mass filter operation.

**Formal Solution to Mathieu Equation**

Solutions to the Mathieu equation for ion motion, Equation 20, can be expressed by

\[ u = a_1 e^{\mu_1 \xi} \sum_{n=-\infty}^{\infty} C_{2n} e^{2in\xi} + a_2 e^{-\mu_2 \xi} \sum_{n=-\infty}^{\infty} C_{2n} e^{-2in\xi} \] (21)

where \( a_1 \) and \( a_2 \) are integration constants which depend upon the initial conditions of ion injection into the field \( u_0 \), \( du_0/dt \), and \( \xi_0 \), \( C_{2n} \) and \( \mu \) are constants which depend solely upon \( a \) and \( q \) and are independent of any initial conditions, and \( n \) is any integer. There are two types of solutions that can result, depending upon the nature of the term \( \mu \). The first of these is the stable solution with bounded values for \( u \) as \( \xi \to \infty \). The second type is the unstable solution where \( u \) increases without limit.
as $\xi \to \infty$. There are four possible cases for $\mu$ that need to be distinguished:

1. $\mu$ is real and nonzero. These solutions have instabilities arising from the $e^{\mu \xi}$ or $e^{-\mu \xi}$ factors.

2. $\mu = i\beta$ is purely imaginary. These are the stable period solutions applicable to the motion of ions in the quadrupole mass filter.

3. $\mu$ is a complex number. Only the trivial case of an ion injected exactly along the field axis ($u_0$, $du_0/dt = 0$) is stable.

4. $\mu = im$ is purely imaginary and $m$ is an integer. These solutions are periodic but unstable.

The second solution type where $\mu = i\beta$ is the only one of interest for the operation of the quadrupole mass filter. For these solutions, Equation 21 can be rewritten as

$$
u = \alpha_1 \sum_{n=-\infty}^{\infty} C_{2n} \cos (2n + \beta)\xi$$

$$+ \alpha_2 \sum_{n=-\infty}^{\infty} C_{2n} \sin (2n + \beta)\xi$$

(22)

Since the type of solution is dependent only on $\mu$, which in turn is dependent solely on the values for $a$ and $q$, then a graphical representation of the stable solutions can be plotted in $a$-$q$ space. Several distinct stability regions result. Some of these stable regions are shown in Figure 3. The only region shown to be empirically useful for quadrupole mass spectrometry to date is that which intersects the $a$-$q$ origin.
Figure 3. Mathieu stability diagram for the mass filter.
The other regions allow maximum ion amplitudes too large to permit quadrupoles of reasonable dimensions and moderate power requirements to be useful.

Mass filter requirements dictate that the ion motion must be stable in both the x and y directions. Let the positive values of a be arbitrarily defined as the x direction. Since the y stability regions differ only by the sign of the a value, the q axis is an axis of symmetry and the y stability regions of Figure 3 are simply reflections of the x stability regions in the q axis. Because of the symmetry between the x and y equations of motion, only half of this region need be considered. This portion, shown in Figure 4, is the most familiar representation of the Mathieu stability diagram. The limits of this stability region occur at $\beta_x = 0$ and $\beta_y = 1$. Iso-$\beta$ contours can be drawn within the stability area and this has been done in Figure 4. This area of both x and y stability is often referred to as the stability or operating region for the quadrupole mass filter. The mass scan line shown will be considered in a later section.

Ion motion under the influence of quadrupolar fields exhibits certain periodic properties. All ions of the same (a,q) value have the same periodic motion. The frequency spectrum of this motion is composed of a fundamental frequency,

$$\omega_{\text{res}} = \frac{\beta}{2} \omega$$

(23)

and higher frequencies,
Figure 4. Mathieu stability diagram near the origin including iso-β contours.
\[ \omega_1 = (1 - \frac{b}{2})\omega; \quad \omega_2 = (1 + \frac{b}{2})\omega, \text{ etc.} \tag{24} \]

Analytical solutions of the Mathieu equations of motions can be rigorously calculated by obtaining values for \(C_{2n}\) using recurrence relationships such as those given by Dawson and Whetten (1968). Berkling (1956) has published coefficient values for \(C_0\) to \(C_6\) as a function of \(q\) and \(\beta\). Approximate solutions can be obtained by neglecting all but the primary frequency of ion motion. The Mathieu equation then becomes analogous to the equation of motion for a simple harmonic oscillator:

\[ \frac{d^2u}{d\zeta^2} + \beta^2u = 0 \tag{25} \]

Solutions to the equations of ion motion are important because they allow trajectories depicting the actual path of an ion in the mass filter to be calculated. Trajectories for a variety of initial conditions have been generated by Brubaker (1967) by numerical integration of the equations point by point using a digital computer. A more versatile approach using matrix methods based on phase-space dynamics has recently been developed (Dawson 1976, pp. 86-92).

Although initial conditions of ion position and velocity do not affect the equations of ion motion in a quadrupole field, they do have a profound effect upon the ultimate performance obtained from a mass filter. The theory derived previously assumed ion injection on the \(z\) axis of the mass filter or \(z\) axis (i.e., \(x_0 = y_0 = 0\)). Any deviation from this perfect injection position results in maximum amplitude
increases equal to the initial position offset value. A more complicated situation arises for ions injected with initial velocity vectors which are not parallel to the mass filter axis. An excellent quantitative treatment of initial conditions has been given by Dawson (1976, pp. 24-31).

The Electrostatic Quadrupole as a Mass Filter

Further consideration of the Mathieu stability diagram of Figure 4 will serve to elucidate both the properties of the electrostatic quadrupole mass filter and the manner in which the mass filter can be used as a mass spectrometer. Figure 5 graphically shows the ion transmission characteristics for the quadrupole mass filter. For any value of \((a,q)\), and hence any stable combination of ac and dc potentials applied to the quadrupole electrodes, a specific operating point within the stability diagram of Figure 4 can be specified. A straight line drawn between the a,q origin and through the stability diagram is known as the mass scan line. The mass bandwidth of the transmitted ions of Figure 5 is determined by the points at which the operating line intersects the two sides of the stability region of Figure 4. This bandpass does, of course, determine the resolution of the quadrupole mass filter used as a mass spectrometer. The slope of the operating line (i.e., the a to q ratio) is generally accepted as a measure of the resolution of the quadrupole mass spectrometer. Two limiting cases are evident. When no dc voltage is applied, the a to q ratio is zero and the quadrupole has no resolution. The mass bandwidth is not infinite, however, since any ions for which q larger than 0.92 will not be
Figure 5. Ion transmission for the quadrupole mass filter.
transmitted. Infinite resolution should be possible when the operating line just passes through the tip of the stability region \((a = 0.23699\) and \(q = 0.70600\)). Since the \(a\) to \(q\) ratio is directly related to the applied ac and dc potentials by

\[
\frac{a}{q} = 2 \frac{U}{V},
\]

the resolution is selected by simply changing the ratio of the applied voltages. The center of the mass bandpass region is determined by the absolute values of \(a\) and \(q\).

In order for the quadrupole mass filter to function as a scanning mass spectrometer, it is necessary that the center mass of the mass bandpass be a variable function of time. This is normally accomplished by allowing the absolute values of \(a\) and \(q\) to increase as a function of time while their ratio is maintained constant. At the output of the mass filter the stable ions transmitted then vary as a function of time. Each succeeding mass ion is brought to stability as the absolute \((a,q)\) values increase. If the \(a\) to \(q\) ratio is maintained constant, the resolution is invariant throughout the entire mass spectrum.

It should be emphasized that in this mode of operation the quadrupole is simply a variable mass transmission filter and not a true mass spectrometer. True spectrometers such as the magnetic sector or time-of-flight instruments separate ions spatially or sequentially so that all of the ions are transmitted through the mass analyzer at all times.
Qualitative Theory of the Quadrupole Mass Filter

The complexity of the rigorous treatment of ion motion in a quadrupole field does not allow for a qualitative understanding of the operation of the quadrupole mass filter. A qualitative approach (Lawson and Todd 1972) to understanding quadrupole theory is useful because it serves to supplement and highlight some aspects that can be obscured by the mathematics of the formal theory.

Consider the effect of the ac field alone on any ion traveling the length of the analyzer. The equations for the x and y components of ion motion (Equations 14 and 15) differ only by a negative sign. This sign difference is of no significance for steady state consideration of the ac term because it merely denotes a 180° phase shift between the application of the alternating potential to the x and y electrodes. The effect of the ac potential on an ion in the quadrupole field is readily assessed when the historical development of the quadrupole is reviewed. The first quadrupole devices (Dayton, Shoemaker, and Mozley 1954) consisted of successive pairs of permanent magnets placed at 90° radially to one another. An ion traversing the field was first compressed toward the axis in one direction and then compressed in a direction perpendicular to the first. The total effect was to produce a strongly focused ion beam. The alternating electrostatic potential serves the same purpose, and it too acts as a strong focusing ion lens.

Now, consider the effect of the dc voltage impressed on the electrodes. The x and y directions must now each be considered separately. A positive ion traversing the quadrupole experiences simple
harmonic motion about quadrupole axis as shown in Figure 6. In the y plane the same positive ion experiences a defocusing force as it is drawn to either of the negatively charged poles as shown in Figure 7.

Finally, consider the combined action of both ac and dc potentials on a positive ion. In the xz plane the addition of the ac potential to the positive dc bias already applied causes the ion to be destabilized. This is not surprising since energy can be stored in a resonant field. Graphically, this case is represented in Figure 8. The addition of ac potential to the negative dc bias of the y poles produces a stabilization of ion motion in the yz plane if the positive cycle of ac potential is sufficient to reverse the y trajectory of the ion. The ion path under these circumstances is shown in Figure 9.

By qualitatively looking at stability as a function of ion mass, an appreciation of the nature of the mass separation of the quadrupole mass filter is realized. Assume that the resolution is such that the bandwidth of the quadrupole is 1 atomic mass unit (AMU). Whenever any ion of mass M is being transmitted by the quadrupole mass filter, heavier ions of mass M+1 and lighter ions of mass M-1 are unstable and are not being transmitted. The lighter ions are unstable in the xz plane because their mass is such that they can respond more readily to the ac field. This ability to "follow" the ac field causes the lighter ions to attain maximum x amplitudes which exceed the field radius of the instrument. Any ion heavier in mass than M is unstable in the yz plane. The momentum attained by such an ion is too large to allow it to "follow" the ac field component sufficiently to compensate for the
Figure 6: Ion trajectory for a positive ion in the xz plane with positive dc potential applied.
Figure 7. Ion trajectory for a positive ion in the yz plane with negative dc potential applied.
Figure 8. Ion trajectory for a positive ion in the xz plane with ac potential and positive dc potential applied.
Figure 9. Ion trajectory for a positive ion in the yz plane with ac potential and negative dc potential applied.
defocusing influence of the negative dc bias potential. Unstable ions pick up an electron by contacting one of the electrodes or their momentum causes them to exit between the electrodes of the quadrupole and be discharged on the grounded housing.

Only the stable ion of mass $M$ has sufficiently balanced forces in both the $x$ and $y$ directions to enable it to pass through the quadrupole without attaining radial displacements exceeding the field radius. This stability has been likened by Dawson (1976) to that of a ball on a saddle. The ball begins to roll down the slope of the side of the saddle, but before it can fall off the saddle inverts. Careful selection of the frequency of the saddle inversion will trap the ball. Another analogy to optical high pass and low pass filters is also helpful. The $xz$ plane functions as a high pass mass filter while the $yz$ plane acts as a low pass. Judicious selection of the $x$ and $y$ voltages will produce a bandpass filter of infinitely variable mass bandwidth.

From the preceding discussion, it is obvious that the left-hand boundary of the stability triangle represents a series of points where the forces toward and away from the axis in the $x$ direction are balanced so that the maximum $x$ amplitude is less than $r_0$. The right-hand boundary represents a similar set of points for the $y$ direction of motion. Continuing along these lines, it is possible to develop a semi-quantitative or approximate approach to quadrupole field calculations. Such a treatment has been reported by Brubaker (1967, pp. 6-9).
CHAPTER 3

THE QUADRUPOLE NOTCH FILTER

Historical Development

The feasibility of the quadrupole notch filter mode of operation was demonstrated by Paul, Reinhard, and von Zahn (1958) shortly after their development of the quadrupole mass filter. They referred to the notch filter as an isotope separator since their intended application involved the separation of isotopes of the same element from one another (i.e., isotope enrichment). This could have been accomplished using the mass filter mode of operation; however, the ion current limit and the transmission characteristics of the mass filter are such that the absolute amounts of each isotope collected were too small to render this method useful. For the notch filter mode of operation, transmission characteristics are much better and ion currents can be a million times greater than those which can be tolerated by the mass filter. Paul et al. (1958) demonstrated the feasibility of the technique using rubidium and sodium as samples. The yields were limited by the drift stability of the then state-of-the-art vacuum tube electronics and the isotope separator could not compete with the gaseous diffusion isotope separations. Paul and coworkers let the project drop and unfortunately, since the original work appeared only in the German literature, there has been little knowledge or discussion of the technique since that time.
Nature of the Notch Filter Separation

In order to understand the notch filter operation, it is necessary to review the frequency spectrum of ion motion discussed earlier. Equation 23 states that the fundamental frequency of ion motion is a function of the frequency of the ac voltage component and the term $\beta$ indicative of the operating point in the stability region. The operating point and $\beta$ are functions of the ac and dc potentials applied to the mass filter. Therefore, the frequency spectrum of ion motion is determined by the applied voltages and is identical for all ions of the same mass to charge ratio.

Consider the trajectory of the ion shown in Figure 10 for which $a = 0$ and $q = 0.55$. The fundamental frequency of ion motion has a period of $9.65\pi$ radians of applied field. Other frequencies of motion are apparent with periods of $2.44\pi$ and $1.66\pi$. If a supplementary resonance field is now applied at a frequency corresponding to the fundamental frequency of ion motion, the trajectory shown in Figure 10 will increase linearly in amplitude with time as the ion absorbs energy from the supplementary field. If the amplitude of the supplementary field is large enough, an otherwise stable ion will be rendered unstable and rejected. If a resonance field amplitude larger than that necessary to reject ions of a single mass is used then ions both higher and lower in mass than the resonating ion will oscillate in the beat frequency. Their amplitudes will also increase, although not as rapidly as the amplitude of the resonating ion. In essence, the voltage amplitude of the resonance field controls the effective mass bandwidth of the
Figure 10. Ion trajectory for the operating point $a = 0$, $q = 0.55$. 
rejection notch. The ion transmission curve for notch filter operation is shown in Figure 11.

Since ions need to be unstable in only one direction to be rejected, the supplementary resonance field does not need to be quadrupolar in nature. A homogeneous field applied in either the x or the y direction is sufficient for operation of the notch filter. This fact greatly simplifies the experimental implementation of the notch filter mode.

Theory of the Notch Filter

The formal theory for the notch filter (Paul et al. 1958, Dawson and Whetten 1968) will be presented below for the case of a homogeneous supplementary field applied only in the x direction. Since it has been previously shown that ion motion in any one direction is independent of motion in either of the other two directions, the only effect of the supplementary resonance field is to modify the Mathieu equation for ion motion in the x direction. The equations of motion for the y and z directions remain unaltered. Under the influence of the homogeneous resonance field, the following inhomogeneous Mathieu equation of motion for the x direction is obtained:

\[
\frac{d^2 x}{dt^2} + \left( \frac{e}{mr_o} \right)(U - V \cos \omega t)x = eE'e^{i\omega't} \tag{27}
\]

This can be contrasted with Equation 14 for ion motion in a simple quadrupole field. The term on the right-hand side of Equation 27
"Isotope Separator" notch filter concept used in the "SAMS" approach

Figure 11. Ion transmission for the quadrupole notch filter.
results from the addition of the homogeneous resonance field. \( E' \) is the resonance field applied in the \( x \) direction at an angular frequency of \( \omega' \). The corresponding canonical Mathieu form of this equation is

\[
\frac{d^2 x}{dt^2} + (a_x' - 2q_x \cos 2\xi)x = ke^{i\frac{\omega'}{\omega}2\xi}
\]  

(28)

where

\[
k = \frac{4eE'}{m\omega^2}
\]

(29)

The general solution of Equation 28 consists of a solution of the homogeneous equation and a particular solution of the inhomogeneous equation. This particular solution of the inhomogeneous equation is physically manifested by an additional oscillation produced by the supplementary field which is superimposed on the original oscillation of the homogeneous equation. Understanding notch filter operation requires that we treat this additional oscillation only. The equation for this oscillation is

\[
X_R = k \left\{ \sum_{n=-\infty}^{\infty} C_{2n} \frac{2i(n + \frac{\omega'}{\omega})\xi}{2i(n + \frac{\beta}{2} + \frac{\omega'}{\omega})} - \sum_{n=-\infty}^{\infty} C_{2n} \frac{-2i(n + \frac{\beta}{2} - \frac{\omega'}{\omega})\xi}{2i(n + \frac{\beta}{2} - \frac{\omega'}{\omega})} \right\}
\]

(30)
In Equation 30, $S_I$ and $S_{II}$ are the basic system of the homogeneous equation and $W$ is the Wronskian determinant. If $\omega' = n' + \beta/2$ is one of the frequencies of ion motion, the resonance solution is obtained:

$$S_{\text{res}} = \frac{k}{W} \left\{ S_{II} \sum_{n=-\infty}^{\infty} C_{2n} \frac{e^{2i(n + \frac{\beta}{2} + \frac{\omega'}{\omega})\xi}}{2i(n + \frac{\beta}{2} + \frac{\omega'}{\omega})} + S_I \sum_{n=-\infty}^{\infty} C_{2n} \frac{e^{-2i(n + \frac{\beta}{2} - \frac{\omega'}{\omega})\xi}}{2i(n + \frac{\beta}{2} - \frac{\omega'}{\omega})} + S_I C_{2n} \xi \right\} \quad (31)$$

At large values of $\xi$, the last term predominates and Equation 31 reduces to

$$S_{\text{res}} = \frac{KC_{2n}}{W} \xi S_I \quad (32)$$

Equation 32 describes an oscillation, the amplitude of which increases linearly with the length of time the ion spends under the influence of the supplementary field. The increased amplitude of ion motion is proportional to the voltage amplitude of the resonance field which is expressed as $E'$. The ion motion amplitude increase is greatest for resonance at the fundamental frequency where $n = 0$.

Now consider the case of an ion close in mass to the ion undergoing resonance amplification. The resonance frequency of such an ion will be near that of the supplementary resonance field being applied. The term of Equation 30 which has the very small denominator predominates. For $\Delta \omega' = (n + \frac{\beta}{2})\omega - \omega'$, the following equation results:
Equation 33 indicates that there is a beat frequency oscillation with an amplitude proportional to voltage amplitude of the supplementary resonance field. The amplitude of an ion motion also increases with its closer approach to resonance (i.e., as the mass difference between the beat ion and the resonance ion becomes smaller).

It is obvious from the preceding discussion that the selection rejection of a single ion with the simultaneous passage of another ion very close in mass to the rejected ion is a delicate operation achieved only by using very stable electronics producing an extremely precise supplementary resonance field.
CHAPTER 4

PERFORMANCE CONSIDERATIONS FOR THE QUADRUPOLE MASS FILTER

Use of Round Rods as Quadrupole Electrodes

Until recently, virtually all work involving quadrupoles was done using mass filters constructed from round rather than hyperbolic electrodes as shown in Figure 12. This modification was necessary because of the difficulty in machining true hyperbolic electrodes. It is extremely difficult to hold the proper tolerances over the entire electrode lengths and when possible the cost of the electrodes is prohibitive. This fact was realized at an early date. In fact, the original work by Dayton et al. (1954) on the magnetic quadrupole strong focusing lens set the stage by using round electrodes and determining the dimensions at which the best approximation to the desired hyperbolic equipotential surfaces were obtained. Best performance is obtained when the field radius, \( r_o \), is adjusted so that

\[
r = 1.148 \ r_o
\]

where \( r \) is the radius of the quadrupole electrode. This value has been, and in some cases still is being, misquoted in the literature as 1.160 instead of 1.148 (Dawson and Whetten 1968, Lawson and Todd 1972).

When round rods are used in place of hyperbolic electrodes, the equipotential surfaces formed in the field region depart slightly from
Figure 12. Common round rod quadrupole filter geometry.
true hyperbolae. These departures or perturbations were studied by Brubaker (1967, pp. 35-37) to determine how ion motion was affected. Round rods reduce the effective \( r_0 \) to about two-thirds of its physical value. The nature of the perturbations involved have been treated by other investigators, but the most illustrative treatment is that of Dawson and Whetten (1969). Third, fourth, and sixth order distortions of the hyperbolic field are considered. They estimated that the sixth order resonance lines resulting from the use of round rods could be significant at resolutions greater than a few hundred atomic mass units. Denison (1971) has suggested that the sixth order distortion can be minimized by using round rods in conjunction with a grounded cylindrical housing of appropriate dimensions. The distortion is negligible when \( r = 1.1468 r_0 \) and the housing radius is \( 3.54 r_0 \).

Brubaker (1967) carried out the only true empirical comparison of round and hyperbolic mass filters. He found that \( r_0 \) must increase by a factor of two if a round rod mass filter is to match the resolution of a similar hyperbolic filter. Since the power required to electronically drive the mass filter varies with \( r_0^4 \), the savings in power affected by a hyperbolic structure cannot be over-emphasized. Brubaker (1967, p. 55) states a hyperbolic quadrupole uses only five percent of the power of a round quadrupole of the same performance.

Unconventional Approaches to Quadrupole Mass Spectrometry

The use of round rods is only one of several approaches to producing quadrupole fields. Blair (1975) has attacked the problem
directly by reporting a design for a milling tool with a straight cutting edge capable of producing hyperbolic surfaces. This process is normally only accurately accomplished using an expensive numerical grinder. The orientation and spacing of the tool with respect to the axis of rotation determine the size of the hyperbola formed.

Other investigators have employed electrode shapes other than circular to produce quadrupolar fields. Hayashi and Sakudo (1968) and Bosi (1974) have investigated the use of circular concave structures to approximate hyperbolic fields. The major advantage of this configuration is that the mass filter construction is greatly simplified. The filter made by Hayashi and Sakudo (1968) was formed by copper plating an accurately machined aluminum cylinder. Glass support rings were then attached to the outside after first making horizontal slots in the plated cylinder. Finally, the aluminum core was dissolved using hydrochloric acid. Performance approaching conventional round electrode analyzers was reported. Sakudo and Hayashi (1975) have also proposed the use of flat-faced electrodes to approximate hyperbolic fields. Computer investigations are reported but no empirical evaluation of the suggestion has yet appeared.

Another novel approach to quadrupole mass spectrometry has been presented by Richards, Huey, and Hiller (1973) who powered a round rod quadrupole mass filter using a rectangular potential waveform instead of the more conventional sinusoidal wave. They found that high resolution could be obtained if a duty cycle of 0.39 was used without any dc voltages being applied. This technique has the advantages of negating
any dependence of the mass separation upon the regulation of the ratio of ac to dc voltages and of obviating the need for any rectification of the ac waveform. Its major disadvantage is that the duty cycle of the rectangular waveform must be extremely well regulated.

**Fringing Field Regions**

Fringing field regions for a quadrupole mass analyzer can be defined as those regions at both the entrance and the exit of the mass filter where weaker fields than those actually impressed upon the electrodes prevail. These fringing fields can be represented by \((a,q)\) values distributed along the mass scan line from the origin to the stability tip, and they result in ion destabilization in the yz but not the xz plane (Brubaker 1967). Consider first the effect of fringing fields at the entrance of the mass filter. In general, fringing fields are detrimental for ions spending more than three or four ac cycles under their influence. Initial conditions of the affected ions are modified so as to introduce an incipient instability in the yz plane (Brubaker 1967). As implied previously, optimum performance can be realized only if considerable care is taken to inject ions into the mass filter as a low divergence beam close and parallel to the z axis of the mass filter. Fringing fields cause a deformation of the ion beam.

The fringing field problem was recognized by Paul et al. (1958) in their early work with the mass filter. Brubaker (1967) was the first to report an extensive study of the problem. His interest grew from the realization that his prototype rocket-borne quadrupole analyzers exhibited poor angular acceptance characteristics in the yz plane. To
counteract the fringing field problems, Brubaker (1967) developed a technique known as the delayed dc ramp. In this method, an auxiliary set of electrodes precedes the mass filter. In the simplest form, these first electrodes are capacitively coupled to the mass filter electrodes so that only the ac voltage component is impressed and the preliminary section serves as a strong focusing lens. Subsequent versions allow for a reduced dc potential in addition to the ac potential, or for just dc bias potentials to be applied to the ramp electrodes. The advantage of the delayed ramp is that the ion remains always in the stable region, thus minimizing effects from entrance fringing fields. The delayed dc ramp also normalizes ion stability in the actual mass filter field so that the phase of the ac voltage at the time of ion entry is not a critical factor. There is, however, some debate in the literature concerning the advantages realized with delayed dc ramp technique. Holme and Thatcher (1972) concluded that the ac phase dependence for a quadrupole mass filter is an important factor only in high resolution work. Austin et al. (in Dawson 1976) state that there is little corroborating evidence to support the improvements Brubaker claims for the delayed dc ramp.

Another approach to efficient ion introduction into a quadrupole mass filter (Marmet 1971, Lefaivre and Marmet 1974) allows most of the ions to be injected when the phase of the ac voltage is near zero. This approach, known as the "bunching box," employs grids biased with a ramped positive dc potential to compress ions for injection at the optimum ac phase. This method has the disadvantage of being optimized for
only one mass at a time and of being of limited utility at high ion cur-
rents. At high resolution, the sensitivity is increased by 125 percent.
The "bunching box" does not counter degradation due to fringing fields.

High resolution requires the optimum ion injection energy to be in the range of 5 to 10 eV (Austin et al., in Dawson 1976). This limits the maximum accelerating voltage that can be used for ion injection and necessitates a compromise between sensitivity and resolution. At low accelerating voltages, resolution is maximized because ions spend more ac cycles in the mass filter quadrupole field. However, they also spend more ac cycles in the fringing fields and this results in a loss of sensitivity, especially for high mass ions. One approach to bypassing this problem is to bias the quadrupole field at a potential other than ground. A large accelerating potential can be used to shorten the time spent by the ions in the fringing fields while high resolution is maintained because the ions decelerate upon entering the biased quadrupole field (Swingler 1968).

Although ion entrance conditions have been discussed widely in the literature, little attention has been drawn to the similar conditions that exist at the exit of the mass filter. Brubaker (1967, p. 20) has shown that ions leave the quadrupole with radial velocities 30 to 40 percent as large as those experienced while traversing the quadrupole. The fringing fields at the exit impart large velocity components to the y direction of motion. Heavy, slow moving ions may actually be reflected back into the mass filter. When a capacitively coupled strong focusing lens is used to terminate the quadrupole field, ion radial velocities
are greatly reduced. Little has been done to modify exit conditions because most quadrupole systems utilize secondary electron multipliers with large surface area dynodes biased so strongly that ion collection is assured. With the widely varied multitude of applications for quadrupoles in recent years, care must be taken to recognize and treat fringing fields at both the entrance and exit of the quadrupole mass filter to ensure good performance.

**Mass Discrimination**

Mass discrimination can be considered to be the mass dependence of the probability for an ion, once formed, to be registered as a transmitted ion at the output of the detector excluding the effects of ionization cross-section and cracking patterns (Brubaker 1969, p. 36). Ideally, any mass spectrometer should exhibit transmission efficiencies which are independent of mass. The most publicized shortcoming of the quadrupole mass filter is its decreased transmission for heavier ions. The topic of mass discrimination has been treated by Brubaker (1969, pp. 36-42). In order to understand mass discrimination, it is necessary to delineate those contributions from the source, fringe fields, mass filter, and detector.

Most simple ions formed in an electron impact ion source retain a velocity equivalent to that possessed by the molecule before ionization. For some complicated molecules, including some hydrocarbons, the ion is formed with more than an electron volt of additional kinetic energy. This extra energy results in decreased detection probability regardless of the type of mass analyzer being used. The probability
reduction for quadrupole mass filters should be smaller than for magnetic analyzers because of the strong focusing character of quadrupole mass separation.

The most severe mass discrimination with quadrupole mass filters occurs during ion transit through the fringing fields between the ion source into the quadrupole mass filter. The forces encountered by ions in this region have been discussed previously. Determined to be the most important aspect of that discussion was the fact that ion transmission decreases with the length of time that an ion spends under the influence of fringing fields. Most quadrupole systems employ a constant accelerating voltage for all masses. This practice results in a decreased velocity (i.e., longer time) for heavier ions traversing the fringing fields between the ion source and the quadrupole. This increased transit time results in decreased transmission efficiency or mass discrimination that becomes more pronounced with increasing ion mass. At constant ion energy, the time spent by the ion in the fringing field region is proportional to the square root of the mass for singly charged ions. One method of minimizing fringing field discrimination effects is to vary the accelerating voltages so that they remain proportional to the transmitted mass. A second method for dealing with the fringing field problem involves the use of the delayed dc ramp technique discussed previously.

A well constructed, normally operating mass filter should not be subject to mass discrimination effects for ions entering along identical trajectories (assuming no effect from fringing fields). For a mass
filter run without proper maintenance to prevent contamination of the electrode surfaces, another type of mass discrimination can occur. For any quadrupole mass filter, it is obvious from the stability diagram of Figure 4 that ions heavier than the stable ones are deposited on the y electrodes and ions lighter than the stable ions are deposited on the x electrodes. At fast scans, the time constant of the insulating layers may be large enough to introduce a field perturbation which is constant at all masses. This perturbation is more serious for light ions where lower applied potentials are used and gives rise to a mass discrimination effect that decreases with increasing ion mass.

The Faraday cup detector displays no mass discrimination. The same statement cannot be made for the secondary emission electron multiplier. For a quadrupole mass filter having constant source accelerating potentials, the axial velocity of an ion leaving the filter is mass dependent. Since the number of secondary electrons formed at the dynode is ion velocity dependent, the output signal of the detector shows a marked mass discrimination for heavier ions. Conventional quadrupoles have been operated at decreased resolution at high mass to compensate for the high mass discrimination caused by fringing fields and electron multipliers.

**Factors Affecting Resolution and Peak Shape**

Before treating resolutions per se, it is first necessary to realize that a complex interdependence exists between the resolution and transmission for any mass filter. Paul et al. (1958) reported early that two distinct regions of quadrupole operation exist. The first of
these, characterized by flat-topped peaks, is obtained at low resolutions where 100% transmission characteristics are obtained. The second region is one where triangular peaks are obtained and transmission is an inverse function of the resolution. Paul et al. (1958) predicted asymmetric peak shapes because of the asymmetry of the stability diagram (Figure 4). Empirically, this situation has not been encountered. A qualitative consideration of the conditions necessary for 100% transmission of ions will serve to put this situation into physical perspective. Two factors interact to give 100% ion transmission. The resolution must be lowered and/or the injection aperture must be minimized. Both of these restrictions limit the maximum radial excursion of stable ions during transit through the mass filter to a distance smaller than the field radius. These considerations are of critical importance when round rather than hyperbolic electrodes are being used. As stated previously, the effective field radius for the round rod mass filter is only two-thirds of the actual field radius, $r_0$.

For operation of a round rod mass filter at less than 100% transmission, the sensitivity is observed to decrease at 1.0 to 1.5 times the rate of resolution increase until $R$ is two or three times the mass. At this point, the sensitivity decreases sixty times faster than the resolution increases (Brubaker and Tuul 1964). All of the preceding facts emphasize that the designer must consider resolution and the compromises it necessitates before embarking upon any mass filter construction.
Precursor peaks are often encountered using conventional quadrupole analyzers employing round rods. Dawson and Whetten (1968) have calculated that small precursors are to be expected at resolutions greater than 200. These precursors can be considered to be a result of the sixth order nonlinear harmonics discussed earlier. Peak splitting at the top of a single mass peak is also routinely encountered with quadrupole mass filters and is usually attributed to defects in the ion source optics or to mechanical misalignment of the mass filter electrodes.

Quantitatively, the resolution, $M/\Delta M$, limit for a mass filter is governed by the number of alternating field cycles to which ions are exposed. This relationship can be approximated by

$$\frac{M}{\Delta M} = R \approx \frac{N^2}{20}$$

(35)

where $N$ is the number of cycles of the ac field and $\Delta M$ is the peak width of mass $M$. The approximation becomes worse with increasing resolution. The number of alternating field cycles an ion experiences is a function of the length of the filter electrodes, $L$, the velocity with which the ion is injected from the ion source into the mass filter, $v_z$, and the frequency of the alternating field, $f$. Equation 35 can be rewritten to express these relationships:

$$R = 0.05 \left\{ fL \sqrt{\frac{M}{2v_z}} \right\}$$

(36)
Resolution, then, increases with the square of the frequency and the length and the first power of the mass. It is observed to decrease as the first power of the ion injection energy.

**Operation of the Mass Filter at Elevated Pressures**

Perhaps the greatest single advantage of the quadrupole mass filter is its ability to operate at increased pressures with little or no performance degradation. This feature is a direct result of the strong focusing nature of the quadrupole field. Magnetic mass analyzers, on the other hand, exhibit increased line broadening (loss of resolution) at elevated pressures. The upper pressure limit of the quadrupole mass filter is ultimately determined by the number of collisions between gas molecules and ions in the analyzer. Linear operation is obtained for pressures up to approximately 10^{-5} torr (Brubaker 1969, p. i). The limit is extremely dependent upon each specific analyzer and especially upon the analyzer length.

Extensive studies were conducted by Brubaker (1969) to determine the effect of a high density of background ions on the performance of the quadrupole mass filter. Specifically, the conditions present during gas chromatographic effluent analysis were approximated. The high density of carrier gas ions contributes greatly to space charging in the ion source by altering the potential distribution. There are two opposing effects taking place simultaneously in the ion source region. Electrons released by the hot filament tend to depress ion source potentials while positive ions formed by electron impact tend to raise ion source potentials. There is a critical pressure where these two effects
counterbalance one another. For Brubaker's (1969) work, this was at a pressure of $2 \times 10^{-3}$ torr. The most important consequence of this for quadrupole work concerns the variability of the ion accelerating voltage which, in turn, affects the mass filter performance. A secondary result is that ion source space charging causes divergence of the ion beam sent to the quadrupole for analysis. This, in turn, alters the initial conditions of ion injection.

A second consequence of high carrier gas pressure occurs in the analyzer region. Stable ions are lost due to collisions with carrier gas neutrals and subsequent charge transfer. The large ionization potential of helium (24.5 eV) renders this effect negligible, but it is an important problem to be considered when doing liquid chromatography-mass spectroscopy (LC-MS). Collisions between light carrier gas molecules and heavier solute and solvent ions can also result in small angle scattering of the heavy ion. Modification of the axial velocity of the ion through the mass filter can result, and in extreme cases the ion may be lost. Although this sensitivity loss is to be expected during high pressure operation, little or no degradation of the resolution will result.

A further complication can arise during high pressure operation when a secondary emission electron multiplier is used as the detector. At elevated pressures, the cascading electrons of the multiplier ionize neutrals in the vicinity which are then collected at the dynode, giving rise to a nonlinear response.
Brubaker (1969, p. 30) determined that performance degradation is apparent at $10^{-4}$ torr with $H_2$. At pressures above $10^{-4}$ torr, performance degrades very rapidly. After substituting a thermal ion source for the electron impact ion source, very little performance degradation was noted at pressures up to $10^{-2}$ torr. This implies that the electron impact source rather than the quadrupole mass filter is the limiting component for high pressure operation in a conventional quadrupole mass spectrometer.

Sample Contamination

The high pressure effects detailed in the previous section dealt ostensibly with high pressures of inert gases. High pressure operation involving organic sample vapors offers added complications arising from sample contamination of the quadrupole electrode surfaces. This is an important aspect, especially for LC-MS work.

Any buildup of sample on electrode surfaces gives rise to local field imperfections. Because of its insulating properties, the contamination layer is prone to building up an electrical charge which perturbs the applied quadrupolar field. Since these perturbations are local in nature, they are less serious than mechanical faults which affect the ion during its entire passage through the mass filter.

No quantitative treatment of contamination has been attempted and it is doubtful that it will be because of the complexity of representing the problem realistically. Scruton and Blott (1973) reported potentials of 400 mV developed by fingerprint impurities. The measurements were made under normal atmospheric conditions, not under vacuum
operation. Another interesting case was reported by Levine and Tobias (1965). Peak splitting occurred during normal operation after the quadrupole had been operated for two years without cleaning. The number of peaks at each mass was observed to increase at higher resolution. Upon disassembly, it was noted that the quadrupole had been mounted so that one pair of electrodes was aligned vertically. The bottom rod of this pair exhibited five dust-like deposits at regular intervals over the 25 cm length of the analyzer when viewed with low angle incident light. The other three rods did not show this and subsequent cleaning of the rods alleviated the problem. The implication is that mounting the mass filter so that the bottom two electrodes are each at 45 degrees from the vertical should serve to reduce any such gravity-aided contamination.

"Zero Blast"

A phenomenon that has become known as "zero blast" occurs when the quadrupole mass filter is operated at the very low applied potentials necessary for the stability of light ions (Dawson 1976, p. 35). The mass filter acts as a strong focusing lens because the diode anode-current characteristic reduces the dc component to zero. The effect is more pronounced for small diameter filters requiring weaker potential fields at very low mass. "Zero blast" could be damaging to the detector at high pressure operation.
"Line of Sight" Photon Noise

In addition to the inherent noise of the electron multiplier, another noise component results because of the straight line geometry of conventional quadrupole systems (Brubaker 1969, pp. 25-28). This noise has been attributed to photons (soft x-ray and ultraviolet radiation) produced in the ion source and to excited neutrals which pass through the analyzer to the detector. Story (in Dawson 1976) proposes that the soft x-rays are formed by a stepwise series of events. First, unstable ions impact on a negative electrode and cause ejection of an electron from the surface. This electron is accelerated by twice the peak ac potential towards the adjacent positive electrode. The impact of the electron causes generation of a soft x-ray from a few to 2000 electron volts in energy. These electrons cause secondary electrons to be emitted if they strike the dynode of the electrode multiplier.

The effect of this line of sight noise is usually to cause a baseline shift which is dependent upon both the ion source emission current and pressure. Nakao (1975) has shown, using argon, that the dark current for on-axis operation, $I_d$, is

$$I_d = 3.5 \, p^{1.1} \, I_e^{1.3}$$  \hspace{1cm} (37)

while that for off-axis operation is

$$I_d = 2.5 \times 10^{-2} \, p^{1.1} \, I_e^{1.3}$$  \hspace{1cm} (38)
where $I_e$ is the ion source emission current. The problem can be especially difficult during analysis of chromatographic effluents where the partial pressure of organic constituents is constantly changing.

Several solutions have been employed in analytical systems. The first of these involves the use of a curved quadrupole to destroy the line of sight relationship between source and detector (Brubaker 1969). The most common solution, however, has been to remove the detector to an off-axis location (Nakao 1975). A third solution that has been suggested involves the use of phase-locked detection. For any mass filter operated at less than 100 percent transmission in the triangular peak region, the output is modulated at the applied ac frequency. Phase-locked detection at this frequency has been suggested but has not been reported (Dawson 1976, p. 27).

**Source Considerations**

Quadrupole mass filters present curious problems in electron optics not usually encountered with other types of mass spectrometers. Proper ion source matching requires a lens system which is more convergent for heavier ions with low axial velocities. The optimum lens is one whose focal length is adjusted as the mass is scanned. Ion source behavior usually depends upon the exit aperture and beam divergence. The ion source lens system for a quadrupole mass filter is often designed to have a final lens aperture radius equal to one-half of the quadrupole field radius in spite of the fact that evidence suggests the use of small apertures for highest resolutions (Brubaker and Tuul 1964). The greatest advantage of the quadrupole mass filter is its ability to
accept nonmonoeenergetic ions. This allows a variety of unconventional ion source types and designs to be successfully incorporated.

Detector Considerations

The two types of detectors commonly used with quadrupole mass filters are Faraday cups and secondary electron multipliers. Faraday cups are the simplest, cheapest, and most reliable detectors but they have a relatively low signal to noise ratio which limits sensitivity and a slow time response which limits scan speed (Austin et al., in Dawson 1976). The slow time response is actually caused by the large amplification factors needed to produce a useful signal. Short leads are necessary to reduce time response and spurious signal pickup. Electrostatic shielding and freedom from vibration are critical for optimum Faraday cup performance.

Electron multipliers offer variable gains as high as $10^7$ with negligible time constant for most gain settings. Disadvantages include the relative instability of the gain and the mass dependence of secondary emission at the dynode which was discussed in the section dealing with mass discrimination.

Three types of electron multipliers are commonly used with quadrupole mass spectrometers. Multistage (usually sixteen) beryllium-copper or silver-magnesium dynode electron multipliers amplify current by having secondary electrons cascade from one dynode to another at a lower negative potential. Continuous dynode electron multipliers use a resistive strip coating in place of physically discrete dynodes. Secondary electrons impact at various points along the length of the strip. The
two major types of continuous dynode multipliers in use are the Magnetic Electron Multiplier (MEM) and the Channeltron. The MEM is the most versatile of all the electron multipliers. It can tolerate numerous recyclings to atmospheric pressure without performance degradation and it is readily cleaned using an eraser. It is, however, physically large, a fact which prevents its use in many vacuum systems. Channeltrons are often used because of their high gain and tolerance of atmospheric recyclings. They are physically smaller than the MEM, but lack its ability to be cleaned. Discrete dynode electron multipliers are widely used but suffer from performance losses after recycling to atmospheric pressure. They are capable of reactivation by heating in an oxygen-rich atmosphere if certain samples such as halogens have not permanently deactivated the surface.
SEPARATOR ANALYZER MASS SPECTROMETRY

Introduction

The Separator Analyzer Mass Spectrometry (SAMS) technique presented in this work represents a unique but straightforward application of the basic principles of quadrupole mass filter operation as described by Paul et al. (1958). A block diagram of the SAMS system components is shown in Figure 13. Between the source and the detector are two electrically isolated quadrupole filters which are the basis for the name of this technique. The quadrupole filter immediately after the ion source is operated in the notch filter mode detailed in Chapter 3, while the filter just prior to the detector is operated as a conventional scanning quadrupole mass filter suitable for mass spectrometric analysis.

The separator quadrupole is purposely drawn larger than the analyzer quadrupole to emphasize the fact that the most efficient operation would be obtained with this configuration. The ultimate design limits of the separator, however, will usually be dictated by the physical size of the vacuum system and power limitations of the separator driver electronics. Although the mass analyzer for the system described in this work employs a quadrupole mass filter, there is no reason why conventional magnetic, double focusing, or time-of-flight mass spectrometers could not be used for mass analysis. Appropriate focusing and
Figure 13. Principal components of the SAMS system.
adjustment of the ion energy at the exit of the separator would, of course, be necessary for optimum results using these other analyzers. Separator length can be varied with the limitation that the ions being rejected must spend approximately one beat period in the supplementary field. This necessitates a compromise between separator length and ion accelerating voltage.

The previous discussion suggests some questions concerning the junction between the two tandem quadrupoles. Tandem quadrupole operation has been reported in the literature by Brubaker (1967) in the presentation of his delayed dc ramp technique. He states that no problems were encountered in transmitting the ions from one quadrupole field to another. However, his filters were driven so that frequency and the phase of the applied ac waveform were the same for both quadrupole sections. Paul et al. (1958) used a second quadrupole to analyze the masses transmitted by the isotope separator quadrupole in their original experiments. In these studies, the two quadrupoles were operated at different ac frequencies -- a situation which closely approximates the operation inherent to SAMS system. No attention was paid to transmission efficiency in this work since only a very small portion of the ion beam was permitted to pass through a tiny orifice in the collector. It is encouraging, however, that no problems were observed.

Qualitative consideration of the region encompassing the exit of the first quadrupole and the entrance to the second can offer some insight into potential problems. As explained in Chapter 3, the notch filter can be considered to be simply a strong focusing quadrupole lens
if no dc potential is applied. The ions, with the exception of those vibrating in the resonance or beat frequencies, are strongly focused into a tight beam along the filter axis. This situation is ideal for efficient injection of the ions into the second quadrupole filter. Two complicating factors which can degrade the transfer efficiency of ions from the separator to the analyzer must be considered. Both of these involve the problem of fringing fields. With two quadrupoles in tandem, the region between the filters is subjected to fringing fields at two distinct frequencies and two distinct voltage amplitudes, one of which is variable with time. The resulting perturbation is a complex function of the two frequencies, the two voltage amplitudes at any instant, the time, the axial energy of ions transmitted by the separator, and distance between the two quadrupoles over which the fringing fields are operative. Such a problem may be amenable to computer treatment using the phase-space dynamics approach as outlined by Dawson (1976).

From a design standpoint, it should be apparent that care must be taken to isolate the separator and analyzer fields while simultaneously placing the two quadrupoles as physically close to one another as possible. Many possible configurations might apply. The first of these involves using a single central support, ignoring the problem, and empirically evaluating the performance. This simple approach may prove to be wholly adequate for analytical work.

Field isolation might best be accomplished by inserting a thin focusing plate between the separator and the analyzer. The plate could be either grounded or biased at an optimum transmission potential. A
time variable dc ramp could be used to best focus each mass. A second approach might utilize a metal tube extending from inside the first field to the inside of the second. Again appropriate dc biasing might be employed. A ramped bias voltage would produce a lens similar to the Turner-Kruger entrance lens used with the Hewlett-Packard 5932A mass spectrometer system.

A more complex system might use a delayed dc ramp operating at the analyzer frequency to ease ion injection into the analyzer quadrupole, and perhaps even a second dc ramp capacitively coupled to the separator quadrupole to control ion exit conditions. A fringe area would still exist between the two dc ramp segments. The analyzer quadrupole must be biased above ground potential to decelerate ions if large accelerator voltages are to be employed for high pressure operation. Since the axis of the quadrupole is positive with respect to the ion accelerating system, ion velocities are decreased at the entrance to the analyzer.

**General Operating Considerations**

Of foremost importance to the operation of the SAMS system is the selection of the operating point for the quadrupole focusing field. Application of only the ac field component will result in the stabilization and strong focusing of all ions having a characteristic $q$ value calculated using Equation 18 such that $0 < q_m < 0.92$. For analytical applications, where the widest possible mass range is necessary, it is desirable to operate the separator with no applied dc potential ($a = 0$) on the electrode. With no dc potential applied, $x$ and $y$ field
amplitudes are identical -- so q will hereafter be used instead of q_m and β in place of β_x or β_y. The relationship between q and β for this condition has been determined by Berkling (1956) to be

\[ q = \sqrt{2} \beta \left(1 - \frac{3}{8} \beta^2 \right) \]  

(39)

This fact is shown graphically in Figure 14. Any applied dc field component increases the resolution of the quadrupole field and consequently narrows the stable mass bandpass of operation. Figures 15 through 17 present calculated values for the low mass cutoff at peak to peak ac voltages up to 5 kilovolts and frequencies of 1, 2, and 4 MHz. The graphs present values for quadrupole filters constructed using 3/8, 1/2, and 1 inch rods, respectively. These values are obtained by combining Equations 12 and 18 and assuming singly charged ions so that the mass to charge ratio, m/e, equals the mass, M, in atomic mass units:

\[ \frac{m}{e} = M = \frac{V}{2\pi^2 r^2 f^2 q} \]  

(40)

Some important conclusions are apparent from these data. When the notch filter quadrupole field is applied at lower frequencies of the order of 1 MHz, the low mass cutoff is very high even for low amplitude fields, effectively rendering important low mass peaks unstable. A comparison of the data for the three different size quadrupole structures shows that the low mass cutoff is decreased drastically by using quadrupole structures of larger field radius. In order to ensure that all masses of interest are stable, it is necessary to choose the size of the
Figure 14. Relationship between $\beta$ and $q$ with no dc potential applied ($a = 0$).
Figure 15. Low mass cutoff as a function of the applied ac potential for a 0.375 inch quadrupole filter.
Figure 16. Low mass cutoff as a function of the applied ac potential for a 0.500 inch quadrupole filter.
Figure 17. Low mass cutoff as a function of the applied ac potential for a 1.000 inch quadrupole filter.
quadrupole structure and the frequency of the applied field so that the low mass cutoff is sufficiently low. It must be remembered that an increase in either frequency or size will result in increased power consumption to produce the same voltage amplitude. Power requirements increase with the square power of the field radius and the fifth power of the frequency. Any addition of dc voltage to the ac quadrupole field will cause a sharp decrease in the stable mass bandwidth in agreement with theory of the quadrupole mass filter.

One additional fact should be mentioned here. The discussions of ion stability so far have been restricted to consideration of the first stability region. There are other regions of mutual x and y stability on the q axis formed by overlap of stability regions other than the first (see Figure 3). The second stability region falls between q values of 7.50 and 7.52. For a 3/8 inch rod quadrupole structure operating at 1 MHz and 102 volts amplitude, diatomic helium ions at mass 4 would be stable. For the same field radius and voltage amplitude at 4 MHz, atomic hydrogen at mass 1 would be stable. Such conditions could prove disastrous if the quadrupole separator field was applied without a supplementary resonance field to remove helium or hydrogen carrier gas ions under the assumption that all ions below the low mass cutoff had been rendered unstable by the quadrupole field alone.

**Ion Resonance Frequency**

It is appropriate at this point to investigate further the factors affecting the fundamental frequency of ion resonance. The primary relationship between the ion resonance frequency and the quadrupole
frequency has already been detailed by Equation 23. Combining Equations 12 and 23 yields

\[ f_{\text{res}} = \frac{\beta}{2} f \]  

(41)

which implies that the fundamental frequency of ion resonance, \( f_{\text{res}} \), is linearly dependent upon the frequency of the applied quadrupole field, \( f \), with a slope of \( \beta/2 \), where the parameter \( \beta \) is indicative of the separator operating point within the stability region. For any given value \((a, q)\), Figure 4 can be used to graphically determine the \( \beta_x \) and \( \beta_y \) values. For the case where no dc voltage is applied, the quadrupole functions as a strong focusing lens, \( \beta_x \) is equal to \( \beta_y \), and the ion motion in the \( xz \) and \( yz \) planes is identical. Figure 14 or Equation 39 can be used to determine the appropriate \( \beta \) values when only ac voltage is applied.

The empirical relationship between the fundamental frequency of ion resonance and the mass is a complex function of the field radius and the voltage amplitude and frequency of the separator quadrupole field. These interdependencies can best be presented by graphical comparisons. Figure 18 presents mass versus resonance frequency data for a 3/8 inch quadrupole operated at 1, 2, and 4 MHz to show the effect of separator quadrupole frequency. The most noticeable aspects are the low mass cutoffs for the 1 and 2 MHz curves which occur at \( M = 128 \) and \( M = 32 \), respectively. This fact could be useful for applications where rejections of all low mass ions are desirable. Only the 4 MHz curve with a low mass cutoff at \( M = 8 \) sacrifices no low mass peaks of general
Figure 18. Resonance mass as a function of the fundamental frequency of ion resonance for a 0.375 inch quadrupole filter at $V_{nf} = 200$ V.
analytical utility. This effect, due to separator quadrupole field instability of the low mass ions, was discussed previously and can be minimized by operation at higher frequencies. As shown by Figure 18, the resonance frequency difference between adjacent unit mass ions decreases more rapidly when higher frequency quadrupole fields are applied. This can be an acute problem for removal of high mass ions with a narrow rejection notch.

Figure 19 investigates the effect of variation in the voltage amplitude of the quadrupole separator field upon the relationship between ion mass and fundamental resonance frequency using a one inch separator quadrupole operated at 4 MHz. Low cutoff mass effects are minimized using the large one inch quadrupole so that they are M = 2, 3, and 12 at peak to peak voltages of 400, 1200, and 4000 V, respectively. The resonance frequency difference between adjacent ions for higher mass is increased at higher quadrupole field voltages. This can be used in conjunction with the improvement at higher frequency noted earlier to produce conditions favorable to high mass ion rejections. The voltage and frequency of the quadrupole separator field are easily adjusted without breaking the vacuum since only simple electronic adjustments of the quadrupole field generator are involved.

Figure 20 examines the effect of the field radius of the quadrupole filter on the relationship between ion mass and the fundamental frequency of ion resonance. The results shown are for an applied quadrupole field of 800 volts peak to peak at 4 MHz and low mass cutoffs are not a problem. Figure 20 illustrates the fact that smaller
Figure 19. Resonance mass as a function of the fundamental frequency of ion resonance for a 1.000 inch quadrupole at $f_{nf} = 4$ MHz.
Figure 20. Resonance mass as a function of the fundamental frequency of ion resonance for various quadrupoles operating at $f_n = 4$ MHz and $V_n = 400$ V.
quadrupole filters provide larger resonance frequency differences between adjacent heavier ions.

A summary of the operating characteristics for the quadrupole notch filter separator shows the importance of selecting the best compromise of quadrupole field radius, frequency, and voltage amplitude for a specific application. It is important to define at the outset what the characteristics of the rejection notch are to be. As Figures 18 through 20 indicate, the factor of prime importance is the mass region in which the rejection notch is to be operated. Single mass rejection becomes increasingly difficult at high mass because the resonance frequency differences for adjacent ions become smaller and the resonance field frequency and voltage amplitude must be more precisely controlled. In addition, both frequency and amplitude drift become factors of critical importance. These considerations finally forced Paul et al. (1958) to abandon attempts at high mass isotope separations.

The analytical applications proposed in this work deal totally with the rejection of ions below mass 200. These fall in the operating region where drift problems are minimized and can be dealt with easily using present day state-of-the-art electronics.

**Operation of the Notch Filter at High Ion Current**

In order to maximize subsequent sensitivity in the analyzer region, it is desirable to put as many ions as possible through the separator notch filter. Since the upper pressure limit for quadrupole operation is determined by space charge effects, the ideal separator would be as large as possible and operate with a very large accelerator
voltage. The upper size limit is determined by the power available to
drive the separator and the considerations discussed previously con­
cerning the relationship between resonance frequency and mass.

Space charging causes distortion of the applied quadrupole
field. Paul et al. (1958) have approximated the influence by assuming
that the space charge density at any point within the notch filter field
radius is constant and proportional to the distance, d, from the center
of the field. The effect of the space charge on the ions can be repre­
sented as a radial force directed at 90° to the quadrupole axis. This
is the same result that would be obtained if a negative dc bias poten­
tial were applied, causing a shift in the quadrupole operating point.
This space charge effect can be represented in terms of a dimensionless
constant, \( a' \), such that

\[
a' = \frac{1.8 \, I}{f^2 \sqrt{M} v_z} \tag{42}
\]

In Equation 42, \( I \) is the ion current through the filter, \( f \) is the fre­
quency of the quadrupole field, \( M \) is the atomic mass, and \( v_z \) is the
accelerating voltage. The operating point is altered so that

\[
a_x = a - a' \tag{43}
\]

\[
a_y = a + a' \tag{44}
\]

Equation 42 can be rearranged to yield
\[ I_{\text{max}} = 0.56 \ a_{\text{max}}' \ f^2 \ \sqrt{Mv_z} \] (45)

This equation can be used to predict the maximum ion current, \( I_{\text{max}} \), that can be put through the notch filter for a given application, the stability limits of which are specified by the maximum operating point perturbation, \( a'_{\text{max}} \), that can be tolerated. For most analytical applications where \( a = 0 \), \( I_{\text{max}} \) should be sufficiently low to render \( a' \) negligible.

As a direct result of the space charge perturbation to the operating point, the fundamental frequency of ion resonance varies with the parameter \( a' \). This problem has been dealt with both theoretically and empirically by Paul et al. (1958) and is not treated in this work since the analytical application involves conditions such that \( a' = 0 \).
CHAPTER 6

DESIGN CONSIDERATIONS

Vacuum System Design

The vacuum system of the Separator Analyzer Mass Spectrometer can be considered to consist of two distinct regions. The analyzer region containing the mass analyzer and the detector is subject to the normal constraints inherent to conventional mass analyzers. When a quadrupole mass filter is used, the pressure in the analyzer region should be kept below $10^{-4}$ torr. In the SAMS system, this requirement can be met by isolating the analyzer section from the separator region using a vacuum flange with a very small aperture to permit ion transit from the separator to the analyzer. A conventional rough pump and baffled diffusion pump will serve adequately for this purpose.

The separator region presents vacuum considerations which are unique for each individual application. Constraints are determined not only by the quadrupole notch filter but also by the type of ionization source employed. Conventional electron impact ion sources are inhibited by pressures greater than $10^{-4}$ torr. Critical ion source potentials are altered by space charging and the source itself is detuned. Closed ion sources with direct pumping to increase conductance might facilitate operation at increased sample loads. The pressure constraints of the
notch filter, discussed in the previous chapter, are determined by space charging effects.

For analysis of gaseous samples, the conductance of the pumping system for the gases being sampled must be able to maintain the pressure in the separator region at a level sufficiently low enough to permit both the source and the notch filter to function properly. A nominal ambient pressure of $10^{-4}$ torr would be ideal. However, improved ion source design would permit operation of the notch filter as high as $10^{-2}$ torr (Brubaker 1969, p. i).

**Mechanical Design Parameters**

The most important mechanical tolerance for quadrupole design has long been known to be the precision with which the four electrodes are located to form the mass filter. The use of round rods to approximate hyperbolic fields introduces another variable into the situation. The recognized relationship between the rod radius and the field radius (Equation 34) has been often misquoted in the literature using the factor 1.60 instead of 1.148, resulting in a 1% error. The performance degradation resulting from this error convinced many users that quadrupole mass filters were not capable of high performance. The problem of rod misalignment has been investigated by Arnold (1970) who determined that the parallelism of the rods, the angle between the x and y axes, and the position of the ion source with respect to the mass filter are all critical for high performance operation.

Quantitative guidelines for quadrupole mass filter construction have been put forth by Paul et al. (1958). The quadrupole should be
assembled so that the field radius conforms to the following constraints

\[ \Delta r_o \leq \left( \frac{0.25}{R} \right) r_o \]  

(46)

The smallest entrance aperture, D, which will give 100% transmission for ions injected parallel to the analyzer axis is given by

\[ D = \frac{r_o}{\sqrt{R}} \]  

(47)

The entrance aperture calculated using Equation 47 does not take into account any perturbations encountered by the ions during their passage through the region of fringing fields.

For the notch filter mode of operation, a much larger entrance aperture can be used because the quadrupole operates at reduced resolution, ideally approaching zero. This larger aperture greatly facilitates the maximization of ion current through the notch filter. Since the notch filter quadrupole is not operated at high resolution, mechanical tolerances are much less stringent than those for mass filter operation (Equation 46).

**Electronic Design Parameters**

The attainable performance using any well-constructed quadrupole mass filter is ultimately limited by the precision with which the driver electronics are regulated. Quantitative guidelines were originally put
forth by Paul et al. (1958) in their classic paper which set limits for the parameters $a$ and $q$, and therefore $U$ and $V$:

$$\Delta a, \Delta q, \Delta U, \Delta V \leq \left( \frac{1}{2R} \right) a, q, U, V$$

(48)

Austin et al. (in Dawson 1976) have stated categorically that the ac and dc power supplies for analytical quadrupole mass filters must be stable to 1 part in $10^4$ (.01%). This is in agreement with the work of Brubaker (1969, p. 47) who has reported that ac/dc ratio variations of 1 part in $10^4$ cause significant transmission losses. This contention has been further proven by Bunyard (Austin et al., in Dawson 1976) who noted that a 30% sensitivity decrease for $^{131}$Xe resulted from a 0.1% increase in the dc voltage. Furthermore, if the ac to dc voltage ratio is not maintained constant over the absolute potential range of the instrument, then the transmission efficiency is no longer independent of the mass (Brubaker 1969, p. 44).

An additional consideration which should be discussed here concerns the rectification of a portion of the ac potential to obtain the dc voltage component. Vacuum tube diode rectifiers are more reliable and are capable of better performance at the high voltage and radiofrequencies commonly used for analytical mass spectrometry than presently available silicon diodes which exhibit nonlinear responses. The use of silicon diodes requires very stringent attention to design criteria, some of which have been enumerated by Austin et al. (in Dawson 1976, p. 146).
Any versatile quadrupole system should include some provision for variation of the ion trajectory energy. The easiest method for doing this involves variation of the ion accelerating voltage. Guidelines for operational values at a given resolution can be obtained from the relationship for maximum accelerating voltage (Paul et al. 1958):

\[ V_{\text{acc}} = 4.2 \times 10^2 \frac{f^2 1^2}{MR} \quad (49) \]

where \( l \) is the analyzer length in meters.

The logical approach to quadrupole mass filter design dictates assessment of the required performance to be expected from the system, especially in terms of resolution and mass range. Mechanical as well as electronic specifications can be derived by calculation and compromise. The most important considerations, filter size and driver field frequency, must be carefully assessed. There is some data to suggest that greater sensitivity and better resolution result for operation at higher frequencies, a factor which has been attributed to the stronger fields necessary to stabilize a given mass ion at higher frequencies (Brubaker and Tuul 1964). This performance gain must be balanced against mass range considerations which are ultimately limited by the available power from a given driver. The power, in watts, required to stabilize an ion of mass, \( M \), is given by

\[ P = \frac{6.5 \times 10^{-4} \cdot CM^2 f^5 r^4}{Q} \quad (50) \]
where \( C \) is the capacitance in picofarads of the mass filter, \( r_0 \) is the field radius in centimeters and \( Q \) is the gain of the oscillator circuit measured at the resonant frequency.

Once again, restrictions on notch filter electronics specifications are not as critical as those for the quadrupole mass filter. The fundamental frequency of ion resonance is dependent upon the frequency and the operating point \((a,q)\) of the applied quadrupole field. The regulation of these parameters can be important, especially in cases where a very narrow mass bandpass notch filter is desired. The control of the frequency and the amplitude of the homogeneous resonance field is also of vital importance for narrow rejection notch applications. The need for regulation of all parameters decreases drastically when a wide-band rejection notch is used for analytical applications such as those described for the SAMS system.
CHAPTER 7

INSTRUMENTATION

Introduction

A block diagram of the experimental system is given in Figure 21. The entire system can be subdivided into three distinct subsystems: 1) the vacuum system; 2) the SAMS system; and 3) the associated electronics necessary to run the system. Much of the vacuum system and quadrupole construction methods are based on work done by Reeve (1971). Each of the subsystems will be considered in detail in the sections which follow.

Vacuum System

Figure 22 details the vacuum system used in all of the studies involving the SAMS system. It represents a compromise in terms of versatility and cost. The vacuum enclosure itself is built using Corning Conical Pipe segments (Corning Glass Works, Corning, New York). The individual pieces are normally joined for vacuum applications by using specially formed Teflon gaskets manufactured specifically for that purpose. Experimental difficulty with vacuum leaks was experienced and butyl o-rings were substituted for the Teflon gaskets throughout the system. Reeve (1971), in using a very similar vacuum system, experienced no leak difficulties while using the Teflon gaskets.
Figure 21. Block diagram of the experimental SAMS system.
Figure 22. SAMS system experimental vacuum system.
Vacuum flanges employed in the system were all of similar design. The original pieces were machined from .375 inch brass plate while later efforts were executed using .600 inch stainless steel plates. The vacuum flanges are secured to the glass ends using 3/8 -16 x 4 inch aluminum bolts and nuts and special aluminum collars. External system connections were formed from 1.375 inch i.d. brass pipe and connecting flanges. The fourline and roughing values used were NRC Model 1251-1 5/8 (Varian/Vacuum Division, Palo Alto, California). The pump stack interface pieces were machined from stainless steel components which were welded into the appropriate configuration.

Pumping speed and vacuum chamber access are the major design considerations of this system. The distance between the vacuum region and the pumps is kept as short as possible. All of the components in the diffusion pump stack were designed to maximize conductance and maintain a linear geometric relationship to the vacuum region in order to improve the pumping efficiency. The major component of the pumping system is a Varian/NRC VHS-6 six inch oil diffusion pump rated at 2400 L/sec for nitrogen. Mounted directly above the diffusion pump is a Varian/NRC six inch cryobaffle which inhibits the backflow of pump oil vapor into the vacuum region. This does cause a decrease in the effective pumping speed to 1300 L/sec, but it is necessary to minimize contamination of the quadrupole filters, the source, and the detector. Finally, a six inch aluminum gate valve (Vacuum Research Corp.) is placed between the pumping system and the vacuum chamber. This permits venting of the vacuum chamber region without pump shutdown and saves an
inestimable amount of time in a research system such as this where frequent modifications are made to components within the vacuum system. The diffusion pump is roughed by a 17.7 CFM Welch Duo-Seal Model 1397 rotary pump.

A Varian/NRC Type 0531 Thermocouple vacuum gauge in conjunction with a Varian/NRC 801 readout system is used to monitor the rough vacuum within the system. High vacuum monitoring is accomplished using a Veeco RG 75P Bayard-Alpert gauge (Veeco Instruments Inc., Plainview, New York) and a Veeco Model RG-81 ion gauge controller.

Instructions for vacuum system pumpdown, venting, and shutdown are given in Appendix A.

Mass Filter Construction

Simple mass filters were constructed using centerless ground stainless steel rods as the electrodes. The insulating holders were machined from a single piece of nylon round stock. A three to five inch length of nylon rod (2.5 inches in diameter) is rounded and faced in the lathe where the center is also located and marked. The piece is then placed in a rotary table mounted on the x-y bed of the mill, the head of which has been previously aligned. Care is taken to ensure that the face to be drilled is parallel with the mill bed and is not "cocked" at an angle. The center is once again located using a center finder or a small starter drill.

Electrode mounting involves jig boring, using the measurement dials provided on the x-y bed of the mill. If care is taken to ensure that a reading is always approached from the same direction to prevent
any error due to gear backlash in the driving mechanism, measurements can be made within ± 0.0002 inches. Once the location of the first electrode hole has been determined, the hole is drilled by starting with a small starter drill bit and progressively enlarging the hole with increasingly larger diameter bits. The final bit used is slightly smaller than the diameter of the rod being used. The final cut is made using a precision reamer (± 0.0001 inches). With nylon, it has been found that the best fit is obtained if the electrode mounting hole is drilled with a reamer 0.001 inches larger than the diameter of the rod to be employed. This is because nylon is flexible and the holes drilled tend to remain at a diameter slightly smaller than the bit size. Mounting holes drilled exactly to size provide a rod fit too tight for convenient and safe assembly of the quadrupole. The method utilized for the quadrupole structures employed in this work used the x and y measurements of the mill bed. After each hole is located and machined, the mill bed is returned to the center of the piece and starting point. The next hole is then located by direct measurement, once again ensuring no error from gear backlash.

The center aperture is then drilled to the appropriate size. This dimension is usually made large since the actual entrance aperture referred to in the theory is determined by the final focusing plate of the ion source or an appropriate mask. Two techniques have been applied to the machining of the center aperture. The first (Figure 23) involves drilling a hole smaller than the field radius and press fitting a stainless steel tube to serve as an injection lens. Without the stainless
Figure 23. Nylon quadrupole mount with drilled center aperture.
steel tube, static charge accumulation on the nylon surface can lower transmission efficiency or inhibit it completely. The second approach (Figure 24) involves boring a center aperture which is larger than the field radius. Since the electrode surfaces are directly exposed to the center region, no stainless steel injection lens is necessary and the ion injection conditions are less restricted. The disadvantage of this method is that some of the support strength of the nylon is sacrificed when portions of the electrode mounting holes are machined away. Critical dimensions for the electrode distances of Figures 23 and 24 are given in Appendix B.

The final step in the machining of the electrode holders is to separate the individual pieces. The finished nylon piece is mounted in the lathe and trued using a dial indicator to 0.0001 inch. The individual mounts are then sliced from the piece using a lathe cutoff tool. Each part must be .75 to 1 inch to maintain strength. For a single quadrupole, only two pieces are needed; for two tandem quadrupoles, three holder pieces are necessary. After a piece is "sliced," it is faced again if necessary and then the stainless steel tube is press fit if the design of Figure 23 is being used. The stainless steel injection lens is cut so that it protrudes approximately .25 inch from each face of a holder. Rods are press fit into one piece, then into the second. Teflon spacers (.0625 inch thick) are punched from sheet material and used as electrical insulators at each end of the structure. They are simply pressed into the electrode holes in the end pieces until they are flush with the nylon face. For the tandem quadrupoles, they are also
Figure 24. Nylon quadrupole mount with bored center aperture.
inserted in the center holder to isolate the two quadrupole rod sets from one another.

This construction has the advantage of minimal cost, simplicity, and intrinsic concentric alignment, but it does present some difficulties. Nylon is flexible and subject to some machining tolerance problems because of its flexibility. Overall errors are usually less than 0.001 inch for an assembled single nylon quadrupole. When a tandem quadrupole is machined, a nylon piece approximately four inches long is necessary. The bits used to drill the electrode holes can exhibit appreciable wander from the true center of the mill head when a piece this thick is drilled. Hole-to-hole distances can vary appreciably and be greater than 0.001 inch in many cases. A second related problem involves the friction heating of the nylon when it is machined. Care must be taken to stop at frequent intervals during the machining of a single hole to allow the piece to cool in order to maintain tolerances.

The final problem just mentioned also suggests the major operating limit of the nylon mounts. They are not amenable to heating and so the vacuum system must be kept at ambient temperature to maintain critical dimensions. This imposes severe restrictions on the nature of the samples that can be used, so that only gases and volatile liquids are acceptable. A solution to this problem is to use machinable ceramic holders. Four identical holders were machined for 3/8 inch electrodes by the Chemistry Department, Professional Shop, University of Arizona, which are appropriate for a heated environment if molybdenum rods are used to replace the stainless steel electrodes presently used. The
temperature expansion characteristics of these materials are almost perfectly matched so that dimensions are maintained at elevated temperatures.

Maintenance of the quadrupole filters involves disassembly and cleaning of the rods in a strong solution of NaOH in an ultrasonic cleaner. The electrodes are rinsed with distilled water and then ultrasonically cleaned in methanol and allowed to dry. The nylon holders have also been cleaned using the same procedure with no evidence of degradation of either the dimensions or the performance. A photograph of a single nylon quadrupole using 1/2 inch electrodes is shown in Figure 25.

**Mass Filter Electronics**

The electronics necessary to operate the quadrupole mass filter can be considered to consist of three basic components: an oscillator, a rectifier, and a regulator. The oscillator designed and built for this work is shown in Figure 26. It is a Class C push-pull design employing 4-400A vacuum tubes which are capable of 1400 watts of radio-frequency (rf) power output with forced air cooling. For the work reported here, high voltage to the plates of the 4-400A tubes is provided by a 1.6 kv unregulated power supply (Fair Radio Sales, Lima, Ohio). External filtering of the voltage is accomplished using a laser discharge capacitor rated at 40 µf and 3 kv (Sargamo Electric Co., Jersey City, New Jersey). Screen grid voltage is supplied by a Lambda Regulated Power Supply Model C-481M-093 (Lambda Electronics, Melville, New York). The filament current is provided by the power supply
Figure 25. Experimental quadrupole filter.
Figure 26. High power radiofrequency oscillator.
detailed in Figure 27. This power supply must float with reference to ground in order for the feedback regulation system to function.

The original solid-state rectifier used for deriving the reference signal from the radiofrequency supply was found empirically to be nonlinear and useless for maintaining the voltage precision necessary for high performance quadrupole mass filter operation. A vacuum tube rectifier, shown in Figure 28, was designed and successfully employed for mass filter use.

The feedback regulator employed for this work is shown schematically in Figure 29. The unit is designed to operate in three distinct ways. Two manual modes are provided, the first of which is subject to regulator control and is controlled by the ten turn potentiometer on the noninverting input of OA2. Nonregulated manual control is accomplished by using the one turn potentiometer which directly drives the output transistor through a 4.7K resistor. The nonregulated mode is essential for balancing the dc outputs of the rf rectifier without fighting the tendency of the regulator to correct for changes. The third mode of operation provides for automatic regulated sweeping of the entire output range of the rf driver. A reference signal is taken from the negative dc voltage at the rectifier and fed to the noninverting input of OA1 through a 3.9 megohm dropping resistor. OA1 serves as a voltage follower and the actual amplitude control is at OA2 where the inverting input follows the noninverting input which is set by the 10 turn manual regulation potentiometer referred to previously or by the sweep generator shown in Figure 30.
Figure 27. Filament power supply.
Figure 28. Vacuum tube rectifier.
Figure 29. Mass filter quadrupole field regulator.
Figure 30. Sweep generator.
The sweep generator simply generates a ramp in the integrator section (OA4). The minimum ramp voltage level (Start Mass) is set by the ten turn potentiometer on the noninverting input of the integrator. The maximum ramp voltage (Stop Mass) is determined by the ten turn potentiometer to the noninverting input of the integrator reset amplifier (OA5). When the stop mass voltage is reached, the 2N1711 transistor turns on and powers the coil of the reset relay which shorts and resets the integrator to the start mass. The SN 555 regulates the capacitor discharge time to prevent relay spot welding. Manual reset can be accomplished at any time using a front panel momentary pushbutton switch. OA6 serves merely as an inverting unity gain amplifier to reverse the ramp direction to provide a positive ramp if ever it is needed. The ±15 volt power supply used to run both the regulator and sweep generator circuitry is shown in Figure 31. The design is simple, inexpensive, and dependable.

Shielded RG-58 coaxial cable was originally used to carry the voltage from the exciter to the vacuum system connectors. The length of the cables (approximately 1 meter) produced sufficient capacitance to affect the rf output. The inner conductor of RG-8 cable was next employed. The capacitance is low and the rf signal is unaffected. The insulation is thick enough to prevent arcing, but the lack of shielding does give rise to some stray radiation. Transmission of the signal to the quadrupole filter is accomplished through Kings KC 79-108 vacuum bnc connectors (Kings Electric Co., Inc., Tuckahoe, New York) in conjunction with bnc to banana adapters.
Figure 31. ± 15 volt power supply.
Notch Filter Electronics

The radiofrequency exciter used to provide the separator quadrupole field is identical to the unit described in the previous section (Figure 26). High voltage is provided by a 1 kv voltage regulated Kepco Model 1250B power supply (Kepco Inc., Flushing, New York); screen voltage by a Lambda Model C-481M regulated power supply; and filament voltage by a Lambda Model LM G3P6-0V-R regulated power supply. No rectifier or feedback regulator was employed. The voltage amplitude was controlled by the abbreviated manual regulation system shown in Figure 32 employing a Heathkit Model IP-18 regulated power supply (Heath Co., Benton Harbor, Michigan) and a 2N1711 transistor. Exact amplitude control is obtained by using the two ten turn potentiometers shown for coarse and fine control of the voltage to the base of the power transistor.

Resonance Frequency Oscillators

Two lower power quadrupole exciter units were utilized as resonance frequency oscillators. The rectification and regulation systems of each were disabled and the voltage amplitudes were controlled by proper adjustment of the plate voltages of each oscillator using Heathkit Model IP-17 regulated power supplies. The first unit was based on the design used in the Finnigan 1015 Commercial quadrupole system, a schematic of which is given in Figure 33. The second resonance frequency oscillator was based on a design used by Reeve (1971) and is schematically depicted in Figure 34. Both of these units are designed to provide output power well in excess of that needed for a homogeneous
Figure 32. Notch filter quadrupole field regulator.
Figure 33. Resonance field oscillator based on a unit designed by Finnigan Corporation.
Figure 34. Resonance field oscillator based on a unit designed by Reeve (1971).
resonance field. However, they were available and easily adjusted to
the proper frequency range by simple alteration of the component values
used in the frequency determining LC tank circuit.

**Isolation Filters**

The most difficult task in implementing the SAMS system involves
the isolation of two oscillators attached to any one electrode of the
separator notch filter. The method by which this is accomplished is
shown in the block diagram of Figure 35. The resonance filters referred
to are merely series LC filters on the outputs of the quadrupole driver.
The inductor and capacitor values are selected so that the circuit
resonates at or near the quadrupole field frequency according to the
following equation:

\[ f = \frac{1}{2\pi\sqrt{LC}} \]  

(51)

The complex filter shown presented more of a design challenge.
The specifications were such that a resonance oscillator at approxi-
mately 0.5 MHz must be effectively isolated from a quadrupole oscillator
operating between 2 and 4 MHz at a voltage amplitude ten times larger
than that of the resonance oscillator. An appropriate design was
developed using general filter design theory (Kaufman and Seidman 1976).
The final complex filter is schematically shown in Figure 36. The
values shown were approximated within five percent during construction.
Two complex filters were built and used with each of the two resonance
oscillators previously detailed. Performance was excellent with a sharp
Figure 35. Block diagram of the experimental system for the notch filter separator.
Figure 36. Complex filter.
frequency cutoff at approximately 1.2 MHz and rejection of more than 99% of the quadrupole field from the resonance oscillators.

Banana leads were used to connect various oscillators and filters, and final connection to the vacuum bnc connectors for the notch filter were again made using the unshielded center conductor from RG-8 cable.

**Ion Source**

The dual filament ion source employed for all of this work is based on a design by Swingler (1970). Figure 37 gives a cross-sectional representation of the source which was assembled using component pieces obtained from ev Ion Optics (Kimball Physics Inc., Wilton, New Hampshire). The design was especially developed for use with quadrupole mass spectrometers and it incorporates a large ionizing volume with no magnetic electron collimation. The ion output beam is focused by an einzel lens to form a small diameter beam suitable for injection into the quadrupole mass filter. Ion acceleration is controlled by the angled back plate which also serves as the electron target. Tungsten mesh is employed to make the repeller plate ion transparent while also maintaining its potential integrity. Filaments are made of 0.100 µm diameter rheniated tungsten wire (Goodfellows Metals Ltd., Esher Surrey, England) which is spot welded to molybdenum pieces which serve as holders.

Ion current control is regulated using the filament current feedback regulator detailed in Figure 38. The design allows for widely variable ion energies and currents by simple adjustment of front panel
Figure 37. Ion source.
Figure 38. Ion source current regulator.
controls. Filament current is provided by an ERA Model TR 36-4 power supply (ERA Trans Pac Corp., Moonachie, New Jersey) which puts out 0 to 36 volts at 0 to 4 amps. The bias voltage is supplied by a Philbrick Researches Model R-100B ± 300 volt power supply. A selection switch is also provided so that either or both of the dual filaments may be operated at any time. Einzel lens potentials are provided by a Philbrick Researches Model R-100B ± 300 volt power supply and the multiple output voltage divider shown in Figure 39. The ion extraction electrode and ion exit aperture are usually operated with -50 to -175 volts, while the ion focus plate is commonly held at ground potential or slightly negative. The ion source connections are made through an eight pin o-ring sealed tube base connector.

The ion source can be totally disassembled for cleaning. Large insulating deposits accumulate after extended analysis of organic vapors. Best cleaning results are obtained if all of the component pieces are ultrasonically cleaned in approximately 5M NaOH followed by a water rinse and ultrasonic cleaning with analytical reagent grade methanol.

**Ion Detection**

Ion detection is accomplished using a Model M306 Magnetic Electron Multiplier (MEM) (Galileo Electro-Optics Corp., Sturbridge, Massachusetts). This multiplier can be exposed to atmospheric pressure repeatedly with no loss of performance and is capable of being disassembled and cleaned. The unit features a continuous glass dynode coated with a mixture of lead and bismuth oxide resistive film which produces gains as high as $10^7$. Ions impact the dynode causing the
Figure 39. Ion source lens potential divider.
emission of secondary electrons which impact the resistive strip several times due to the weak magnetic field surrounding the resistive strip. A cascade amplification effect is produced since each electron impact generates additional secondary electrons. A high voltage of -2.2 kilovolts is provided by a Carad #1524 H.V. Precision 3 kilovolt power supply. Four voltages are actually needed to operate the MEM and these are produced by a carbon resistor voltage divider mounted within the vacuum system. The high voltage is supplied to this internal divider through a flange mounted vacuum bnc connector. This voltage divider is shown schematically in Figure 40.

The cascading electrons are ultimately collected at the anode and the resulting current is fed through a flange mounted vacuum bnc connector to an electrometer for measurement. The electrometer used for this purpose is schematically shown in Figure 41. A high impedance 534 FET input operational amplifier is the key component. Gain and capacitive filtering are provided by the front panel rotary switches shown. Offset voltages as high as ± 15 volts dc can be applied to counteract any baseline shift. The output of the electrometer is recorded using either a strip chart recorder or an oscilloscope.

Test Equipment

All ac and dc voltage measurements were made using a Hewlett-Packard Model 410C voltmeter. Applied ac waveforms were monitored using a Type RM 45A Tektronix oscilloscope. Ion detection output was monitored using a Type 564 Tektronix storage oscilloscope.
Figure 40. Detector supply potential divider.
Figure 41. Electrometer.
CHAPTER 8

EXPERIMENTAL RESULTS FOR CONVENTIONAL MASS FILTER OPERATION

Introduction

It should be stressed at the outset of this section that the early operation of this quadrupole system represented a learning experience for the investigator. The open literature is notably lacking in information concerning the practical operation of quadrupole mass filters. This one fact has probably been the major deterrent discouraging more researchers from constructing their own quadrupole systems. The recent publication of Quadrupole Mass Spectrometry (Dawson 1976) evokes both encouragement and disappointment. This work is, by far, the most complete published to date, but it is inclined more toward an esoteric consideration of the quadrupole mass filters at the expense of some of the more practical aspects of mass filter design and operation.

In retrospect, some of the experimental approaches utilized in this work may seem somewhat naive when compared to the methods applied later using the SAMS system. However, they significantly contributed to the establishment of the performance of the experimental system as a viable and useful quadrupole mass spectrometer.

Acquisition of Conventional Mass Spectra

The first problem to be faced was the mounting of the source, mass filter, and detector within the vacuum system. A 15 inch aluminum
The mass filter used in these studies, shown in Figure 25, utilized nylon holders and .5 by 12 inch rods. No ground shield housing was employed, but a grounded ion injection lens was used. The detector high voltages were generated external to the vacuum system and four vacuum bnc connectors were used to pass the necessary bias voltages to the detector inside the vacuum system. The vacuum system itself consisted of only one glass "T" section and was operated without the cryo-baffle used in later work. Residual gas pressures of $6 \times 10^{-6}$ torr were common.

**Mass Spectra of Organic Vapors**

The analyses of most organic vapors require some type of heated sample delivery system to prevent sample condensation and contamination of the system components. A heated expansion volume (HEV) was constructed using a 250 ml gas sampling bottle, a Teflon quick connect, a needle valve, Swagelok fittings (Crawford Fitting Co., Cleveland, Ohio), and heating tape. The final design is represented in Figure 42. The gas sampling bottle serves as a sample reservoir and the needle valve meters the amount of sample delivered to the vacuum system. The entire
Figure 42. Experimental sample delivery system.
system is wrapped with heating tape which is run by a Powerstat Variable Autotransformer Type 116B (The Superior Electric Co., Bristol, Connecticut).

The spectra were recorded using a Heath Model EU-208 strip chart recorder (Heathkit Co., Benton Harbor, Michigan). Typical results obtained are represented by the mass spectrum of toluene (Figure 43). Unit resolution is apparent out to approximately mass 100; however, the intensity of the higher mass peaks is lower than expected. This indicates that high mass discrimination is occurring. This problem will be discussed further in a succeeding section. These results were encouraging, however, since acceptable mass spectra were produced.

Gas Chromatography-Mass Spectrometry Operation

The analysis of the total effluent of a packed column gas chromatograph was next achieved by interfacing the quadrupole mass spectrometer directly to a Carle Basic gas chromatograph (Carle Instruments Inc., Fullerton, California). This was done in such a manner that the HEV delivery system was left intact. The effluent of the GC was diverted at the output end of the column before passage through the thermal conductivity detector and sent directly to the mass spectrometer for analysis. The transfer lines were wrapped with heating tape to prevent sample condensation and minimize peak spreading.

Specific ion detection (SID) was attempted using toluene as the sample to be detected. SID involves operating the mass spectrometer in a static nonscanning manner so that only ions of one stable mass are detected. Toluene is an ideal sample for this purpose because of the
Figure 43. Spectrum of toluene.
intense peak it exhibits at mass 91 which is formed by loss of a proton from the parent ion to yield the resonance stabilized tropylium ion.

The analysis was carried out using a 5 foot, 8% dinonyl phthalate, 1/8 inch packed column (Carle Instruments Inc.). The helium carrier gas was adjusted to a flow rate of 40 mL/min measured with a bubble meter at atmospheric pressure and the column temperature was maintained at 110°C during the analysis. Standard solutions were prepared by serial dilution from a 10% stock mixture by volume of toluene in the solvent of choice. Studies were conducted employing methanol, benzene, and dimethylsulfoxide (DMSO) as solvents.

The mass spectrometer output was adjusted to mass 91 using a toluene sample leaked from the heated expansion volume. The exact mass location was empirically set by using the manual regulated mode of operation to vary the mass value slightly until the maximum output signal was observed. Initial efforts using methanol and benzene as solvents were characterized by large output signals for the solvent peaks as well as for toluene sample peak. Since neither of these solvents can be expected to produce a mass 91 peak, these results were unexpected. At the time, impurities in the solvents were suspected; however, subsequent investigations using conventional chromatographic detectors disproved this theory. Several additional solvents were investigated and it was found that the effect was minimal with DMSO. Standards were prepared and used immediately with the most dilute being analyzed first to maximize the signal to noise ratio and minimize memory effects.
The results of this experiment are presented in Figure 44 as a log-log plot of detector current versus the sample weight in grams of toluene injected on column. The linear dynamic range of the analysis was six orders of magnitude and the minimum detectable quantity of 87 picograms was limited by the system noise.

**Modification of the Conventional Operating System**

These initial studies served to point out both the capabilities and the shortcomings of the experimental quadrupole system. The ion source alignment using the helium-neon laser is a tedious procedure, the results of which are often negated by vacuum system vibrations disturbing the ion source alignment during operation. A new procedure was devised for mounting the ion source directly to the front holder of the mass filter. Holes were drilled in the front holder to exactly accommodate the four ceramic rods which support the ion source components. Alignment errors of ± .002 inch are obtained using this method. This technique proved very successful for the precise and reproducible alignment of the ion source with the mass filter entrance and it was employed in all succeeding studies.

The minimization of fringing field effects, which caused the high mass discrimination apparent in Figure 43, necessitated more extensive system changes. The entire quadrupole mass filter was shielded using a grounded aluminum pipe. Holes were drilled along the length of the shield pipe to permit sufficient pumping of the analyzer region during operation at elevated pressures. The mass filter cannot be fastened to the housing or warping of the quadrupole structure will
Figure 44. Working curve for toluene using specific ion detection at mass 91.
result. Therefore, the housing is mounted to the optical bench and the quadrupole is allowed to freely slip-fit into the housing. Aluminum end caps are pressed into the housing to shield high frequency radiation from the source and detector. These modifications greatly reduced the effects of mass discrimination and were retained for all future work.

The signal generated by the solvent peak during the GC-MS experiments was determined to be mass independent and directly related to the filament emission current. This noise was finally attributed to photons produced in the ion source, a problem which has been noted by other researchers and treated in a prior section. Location of the detector off-axis from the mass filter exit is recommended to minimize the photon noise level. A geometry similar to that reported by Nakao (1975) was implemented and the photon noise was decreased by two orders of magnitude. This configuration is recommended for all studies involving chromatographic effluent analysis or operation at elevated pressures.
CHAPTER 9

EXPERIMENTAL RESULTS FOR SEPARATOR ANALYZER

MASS SPECTROMETRY

Introduction

Since this work introduces a mass spectrometric technique that is both unique and untested, most of these initial experiments are concerned with empirical characterization of the concepts and performance capabilities of the method rather than with direct applications. The implications and projected applications of the SAMS technique are discussed in more detail in the next chapter.

In most analytical mass spectrometric applications, the rejection of low mass ions is desirable because quantitative procedures are usually applied to the more characteristic high mass ions. For gas chromatographic and environmental samples, the rejection of some or all ions below mass 50 is sufficient for most applications since the organic samples usually involved produce similar fingerprint spectra in that region. For liquid chromatographic samples, rejection of all ions below mass 100 to 200 is called for to eliminate the ions due to the solvent. Little cogent information is normally sought in this region for the compounds usually analyzed by HPLC. The experimental results presented here are almost totally restricted to masses below 50 in keeping within the areas of analytical interest and present experimental configuration
vacuum system limitations. Residual gas ($N_2$, $O_2$) has been studied in detail since it has the advantage of not requiring a precise sample delivery system and the residual leakage of the vacuum system is relatively constant (residual gas pressure = $2 \times 10^{-5}$ torr) and free of short-term variations.

The experimental system utilized for the SAMS studies incorporates the extended vacuum system shown in Figure 22 and two .375 x 12 inch quadrupoles mounted in tandem using nylon holders with bored centers. Both of the quadrupoles and the ion source are shielded by an aluminum pipe drilled to aid pumping. Sample delivery from the heated expansion volume is made directly to the ion source enclosure region through a .125 inch stainless steel tube. The quadrupole notch filter and mass filter electronics are implemented as shown in Figure 35.

The notch filter mode of operation is ultimately a function of five interdependent variables: the frequency and amplitude of the quadrupole notch filter field, the frequency and amplitude of the homogeneous resonance field, and the ion accelerating voltage. In this work, the accelerating voltage is maintained virtually constant so that the results observed are a function of the nature of the applied notch filter and resonance fields. It is the relationships among these four variables that are investigated in this work. All of the theoretical calculations made throughout the presentation use only four of the relationships detailed previously:

$$\omega = 2\pi f$$

(12)
The calculation of \( g \) values, the \( q \) value for any mass, \( q_m \), the ion resonance frequency, \( f_{\text{res}} \), and the resonance mass, \( M_{\text{res}} \), are accomplished in this way. All of the voltage readings presented refer to peak to peak values.

**Characterization of the Notch Filter Quadrupole Field**

With only the ac voltage component of the quadrupole field applied, the separator portion of the SAMS system functions as a strong focusing lens. The ion stability is a function of the \( q \) value of the operating point which, in turn, is related to the ac voltage amplitude as described in Equation 18. Initial experiments were concerned with the empirical verification of this fact. The first study conducted used residual gas as the sample. The mass filter was operated at 2.25 MHz and tuned for unit resolution throughout the mass range and the notch filter was run at 2.06 MHz with no applied dc voltage. The results are presented in Figure 45. The log of the detected current is plotted versus the \( q \) value for ions at masses 14 and 16 and 28 and 32 which are predominantly formed from monatomic and diatomic nitrogen and oxygen. The ion source was operated at an ion current of 500 microamps, an accelerator voltage of +125 volts, and a filament bias voltage of -10 volts.
Figure 45. Ion transmission for residual gas as a function of $q$. 
The maximum ion transmission is obtained at q values lower than the 0.6 value predicted by theory. This fact might be attributed to the weak fields produced by the ac voltage amplitudes necessary to focus the low mass ions at this frequency. However, the maximum transmission q value decreases with increasing ion mass. This suggests that fringe field perturbations between the source and the separator are significantly decreasing ion transmission. In keeping with the predicted theory, a sharp drop in ion transmission is observed as a q value of 0.92 is approached. As indicated previously, at this limiting q value, the amplitude of ions injected on the z axis becomes larger than the instrument field radius.

A second study was carried out using carbon tetrachloride as the sample. The mass filter operating frequency was 2.12 MHz and unit resolution. The notch filter frequency was 1.92 MHz. The ion current was set at 500 microamps with an accelerator voltage of +165 volts and a filament bias of -10 volts. The results for some carbon tetrachloride and residual gas ions are presented in Figure 46. The upper limit for notch filter voltage amplitude is determined by the high voltage supply which, for this work, was 1 kilovolt. Once again maximum ion transmission is observed at q values lower than predicted and sharp transmission cutoffs are obtained as the limiting q value of 0.92 is reached. The \( \text{N}_2^+ \) and \( \text{CCl}_2^+ \) ions as masses 28 and 82, respectively, were observed to exhibit rather broad transmission curves. The reason for this is not clear.
Figure 46. Ion transmission for carbon tetrachloride and residual gas as a function of $q$. 
Another factor that may contribute to the shift in maximum ion transmission to lower q values is radiative coupling between the mass filter and the notch filter. Experiments were conducted to measure the degree of cross-coupling between the two quadrupole fields. With the notch filter at a frequency of 2.06 MHz, the voltage amplitude was varied and the voltage radiated to the mass filter was measured at the flange connector. The experiment was repeated with the mass filter at 2.23 MHz and the amplitude of the voltage transmitted to the notch filter was measured. The results for mass filter and notch filter quadrupole cross-coupling are presented in Figures 47 and 48. Cross-coupling of the homogeneous resonance field to the remaining two notch filter electrodes and to the mass filter electrodes was evaluated at a resonance frequency of 0.170 MHz and is presented in Figure 49. A quantitative treatment of cross-coupling is extremely difficult because of the frequency difference between the two quadrupole filters.

**Single Ion Rejection Studies**

Rejections of single residual gas ions were conducted in a manner similar to the original isotope separator experiments reported by Paul et al. (1958). Figure 50 presents typical residual gas spectra with and without the homogeneous resonance field applied. Figure 50A shows the residual gas spectrum with the resonance field applied to remove diatomic nitrogen ions at mass 28. Figure 50B shows the residual gas spectrum for the same experimental conditions without the applied resonance field. Single ion rejections were carried out for each of the monatomic and diatomic nitrogen and oxygen ions using a single resonance
Figure 47. Radiative cross-coupling from the analyzer to the separator.
Figure 48. Radiative cross-coupling from the separator to the analyzer.
Figure 49. Radiative cross-coupling from the homogeneous resonance field to the adjacent notch filter-electrodes and to the mass filter.
REMOVAL OF $N_2^+$

Figure 50. Single ion rejection of $N_2$ using the SAMS system.

A. With the applied resonance field. B. Without the applied resonance field.
oscillator. These data are presented in Table 1. The mass filter was operated at 2.22 MHz and unit resolution and the notch filter was run at 4.20 MHz and 325 volts peak to peak. The ion current was set at 500 microamps, the accelerator voltage at +125 volts, and the filament bias at -10 volts. A parameter called the Rejection Ratio, \( R_{\text{rej}} \), defined as the ratio of the ion intensity with the resonance field applied to the ion intensity without the resonance field, is presented. \( R_{\text{rej}} \) actually corresponds to the fraction of ions transmitted through the notch filter. Single ion rejection of more than 99% of the mass 28 and mass 32 ions is accomplished without affecting the rest of the spectrum. Approximately 95% of the monatomic ions at masses 14 and 16 were rejected, but some loss of the adjacent ions was observed in each case. Feedback regulation of both the notch filter oscillator would probably also reduce these residual effects. However, since the major analytical interest centers around the rejection of ions of a band of masses rather than ions of a single mass, these modifications have not been incorporated into the experimental system.

**Multiple Ion Rejection Using a Single Oscillator**

As indicated in Chapter 3, the width of the rejection notch is increased as the voltage amplitude of the resonance field is increased, since ions both heavier and lighter than the resonating ion oscillate in the beat frequency and are rejected. This situation was investigated empirically using residual gas as the sample and the results are presented in Figure 51. For this experiment, the mass filter was operated at 2.23 MHz, the notch filter quadrupole field at
Table 1. Single ion rejection ratios using residual gas as the sample.

<table>
<thead>
<tr>
<th>Mass eliminated</th>
<th>Rejection ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m/e 14</td>
</tr>
<tr>
<td>14</td>
<td>0.0563</td>
</tr>
<tr>
<td>16</td>
<td>0.613</td>
</tr>
<tr>
<td>28</td>
<td>0.963</td>
</tr>
<tr>
<td>32</td>
<td>1.01</td>
</tr>
</tbody>
</table>
Figure 51. Mass width of the rejection notch as a function of the resonance field voltage amplitude.
4.24 MHz and 339 volts peak to peak, and the notch filter resonance field at .340 MHz which corresponds to ion resonance at mass 24.8. Spectra were alternately obtained with and without the applied resonance field to minimize long-term drift effects. It is readily apparent that small resonance field voltage amplitudes are sufficient to reject wide bands of ions. In fact, an auxiliary field amplitude of 25 volts peak to peak is sufficient to remove virtually all of the residual gas ions. The implication is that the SAMS system can be applied to analytical applications requiring wideband ion rejection by using low power solid-state resonance field oscillators.

This conclusion is further emphasized by the data in Tables 2 through 5 which detail experiments designed to remove masses 28 through 32 while minimally affecting masses 14 through 18. Typical experimental spectra for the data of Table 2 are shown in Figure 52. Figure 52A shows the residual gas spectrum with the resonance field while Figure 52B shows the same spectrum without the resonance field. Ions at mass 18 are primarily due to water in the system. Ion source operating conditions approximated those reported for previous studies and the mass filter was run at 2.23 MHz and unit resolution. The notch filter quadrupole field frequency was varied from 4.24 MHz to 2.498 MHz. The amplitude of the notch filter quadrupole field was adjusted so that the operating point (q value) was roughly equivalent for each of the experiments.

Generally, the most efficient ion rejection was achieved by higher notch filter quadrupole field frequencies. Table 2 gives data
Table 2. Rejection ratios for wideband removal of \( \text{N}_2 \) and \( \text{O}_2 \) (\( f_{nf} = 4.24 \text{ MHz} \), \( V_{nf} = 170 \text{ V} \), \( f_{res} = 0.287 \text{ MHz} \), \( V_{res} = 8.48 \text{ V} \)).

<table>
<thead>
<tr>
<th>Mass</th>
<th>( R_{\text{rej}} )</th>
<th>( 1/R_{\text{rej}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>1.07</td>
<td>0.934</td>
</tr>
<tr>
<td>16</td>
<td>0.916</td>
<td>1.09</td>
</tr>
<tr>
<td>17</td>
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<td>18</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>28</td>
<td>0.000371</td>
<td>2700</td>
</tr>
<tr>
<td>32</td>
<td>0.000740</td>
<td>1350</td>
</tr>
</tbody>
</table>

Table 3. Rejection ratios for wideband removal of \( \text{N}_2 \) and \( \text{O}_2 \) (\( f_{nf} = 2.92 \text{ MHz} \), \( V_{nf} = 138 \text{ V} \), \( f_{res} = 0.170 \text{ MHz} \), \( V_{res} = 4.64 \text{ V} \)).

<table>
<thead>
<tr>
<th>Mass</th>
<th>( R_{\text{rej}} )</th>
<th>( 1/R_{\text{rej}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.989</td>
<td>1.01</td>
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<td>16</td>
<td>0.868</td>
<td>1.15</td>
</tr>
<tr>
<td>17</td>
<td>0.789</td>
<td>1.27</td>
</tr>
<tr>
<td>18</td>
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<td>1.22</td>
</tr>
<tr>
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<td>667</td>
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<tr>
<td>32</td>
<td>0.00165</td>
<td>606</td>
</tr>
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</table>
Table 4. Rejection ratios for wideband removal of N\textsubscript{2} and O\textsubscript{2} ($f_{nf} = 2.92$ MHz, $V_{nf} = 158$ V, $f_{res} = 0.170$ MHz, $V_{res} = 6.22$ V).

<table>
<thead>
<tr>
<th>Mass</th>
<th>$R_{rej}$</th>
<th>$1/R_{rej}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.961</td>
<td>1.04</td>
</tr>
<tr>
<td>16</td>
<td>0.862</td>
<td>1.16</td>
</tr>
<tr>
<td>17</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>18</td>
<td>1.08</td>
<td>0.926</td>
</tr>
<tr>
<td>28</td>
<td>0.0198</td>
<td>50.5</td>
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<td>32</td>
<td>0.000743</td>
<td>1340</td>
</tr>
</tbody>
</table>

Table 5. Rejection ratios for wideband removal of N\textsubscript{2} and O\textsubscript{2} ($f_{nf} = 2.50$ MHz, $V_{nf} = 113$ V, $f_{res} = 0.160$ MHz, $V_{res} = 7.50$ V).

<table>
<thead>
<tr>
<th>Mass</th>
<th>$R_{rej}$</th>
<th>$1/R_{rej}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.913</td>
<td>1.09</td>
</tr>
<tr>
<td>16</td>
<td>0.892</td>
<td>1.12</td>
</tr>
<tr>
<td>17</td>
<td>0.886</td>
<td>1.13</td>
</tr>
<tr>
<td>18</td>
<td>0.891</td>
<td>1.12</td>
</tr>
<tr>
<td>28</td>
<td>0.00909</td>
<td>110</td>
</tr>
<tr>
<td>32</td>
<td>0.00963</td>
<td>104</td>
</tr>
</tbody>
</table>
Figure 52. Multiple ion rejection of $\text{N}_2$ and $\text{O}_2$ using the SAMS system.

A. With the applied resonance field. B. Without the applied resonance field.
for the highest frequency studied, 4.24 MHz. More than 99.9% of the ions at masses 28 and 32 are removed by an 8.48 volt resonance field. The reciprocals of the rejection coefficients are also given to provide another perspective on the power of the SAMS technique. For mass 28 of Table 1, the implication is that for every 2700 ions that reach the detector without the field applied only one is transmitted to the detector with the resonance field applied. Examination of Tables 3, 4, and 5 suggests that more efficient ion rejection is obtained at higher frequencies. This fact may be related to the higher voltage amplitudes necessary to maintain the same operating point at higher frequencies.

As mentioned previously in discussing mass filter operation, performance seems to be improved at higher frequencies. More efficient ion rejection at lower frequencies might be obtained using larger quadrupole filters.

Tables 3 and 4 present data for two experiments at the same notch filter and resonance frequencies. The notch filter amplitude was varied to shift the resonance mass and the resonance amplitude was empirically adjusted until a transmission decrease of the lower mass residual gas ions was noted. The ion rejection for masses 28 and 32 are roughly equivalent for a $M_{\text{res}}$ of 29.0 (Table 3). However, when the resonance mass is shifted to 33.2 (Table 4), rejection of mass 32 ions is enhanced at the expense of mass 28 ion rejection. This comparison emphasizes the importance of empirically tuning the rejection notch with the aid of an oscilloscope rather than blindly depending upon calculated theoretical values. The poorest rejection coefficients were obtained at
the lowest frequency of 2.498 MHz (Table 5). These values were more than a factor of 10 below those obtained at the highest frequency.

A final experiment was run in which the resonance field frequency and amplitude and the notch filter quadrupole field frequency were held constant. The notch filter quadrupole field amplitude was varied sequentially and the effect on the ion transmission of masses 28 and 32 was recorded. The results and the experimental field parameters are given in Figure 53 where absolute ion intensity (amps) is plotted versus the notch filter quadrupole field amplitude. The rejection notch curves for masses 28 and 32 are readily apparent. The ion current would be expected to be constant on both sides of the rejection notch. This effect is observed at high field voltages, but is not apparent at low field voltages. The weak field strength inherent to low notch filter quadrupole field amplitudes is thought to be the cause of this decreased ion transmission.

**Ion Rejection Using Two Resonance Oscillators**

Paul et al. (1958) suggested, but never verified, that two homogeneous resonance fields could be applied simultaneously, each to different pairs of electrodes, to reject ions in two regions of the spectrum without affecting the rest of the spectrum. This capability was explored using carbon tetrachloride from the HEV as the sample. Only the spectral region below mass 60 was considered. The notch filter was operated at 3.70 MHz and 354 volts peak to peak, and the mass filter at 2.23 MHz. Ion current was maintained at 500 microamps, accelerator voltage at +125 volts, and filament bias at -10 volts. One resonance
Figure 53. Ion current for N₂ and O₂ as a function of notch filter quadrupole field voltage amplitude at constant resonant field parameters.
oscillator was set to 6.2 volts at 0.321 MHz and the other to 4.7 volts at 0.669 MHz. These correspond to resonance rejections at masses 31.3 and 15.6, respectively. The purpose of this experiment was to reject as many of the residual gas ions as possible while transmitting the greatest percentage of the Cl$^+$ (m/e 35,37) and CCl$^+$ (m/e 47,49) as possible. With a single oscillator, it is very difficult to reject many of the residual gas ions without severely reducing the intensity of the sample peaks, especially those at m/e 35 and 37. With two resonance oscillators, a large fraction of the residual gas ions can be rejected as shown in Figure 54. Other applications of two oscillator resonance rejection might include the analysis of intermediate mass ions while rejecting ions which are both lighter and heavier.
Figure 54. Wideband mass rejection using two independent homogeneous resonance fields.
CHAPTER 10

FUTURE DEVELOPMENT OF THE SAMS SYSTEM

Vacuum System Modifications

The first and most important modification to be made to the existing experimental system is the implementation of differential pumping of the separator and analyzer regions as detailed in Figure 55. The present system will require another 6 inch high speed oil diffusion pump, cryobaffle, and gate valve. In addition, a special flange having o-ring grooves on both faces and a very small central aperture which can be aligned for maximum ion transmission is needed. This flange would also serve to reduce radiative coupling between the separator and analyzer regions.

The second important modification to the vacuum system is the incorporation of some unit for heating the vacuum chamber, preferably one equipped with thermostatted control so that temperature can be accurately set and maintained. The glass of the vacuum system is rated for use at temperatures up to 450°F.

The nylon quadrupole mounting holders are not acceptable for operation at higher temperatures because the large coefficient of thermal expansion for nylon causes large dimensional errors in the quadrupole structure at higher temperatures. One solution to this problem is the use of ceramic holders and molybdenum rods which have offsetting
Figure 55. Proposed differentially pumped vacuum system.
coefficients of thermal expansion that allow precise maintenance of critical dimensions at temperatures other than ambient. A set of four ceramic holders has been machined and is ready for use.

Performance Evaluation at Elevated Pressures

Once the vacuum system has been modified to provide differential pumping and to operate at elevated temperatures, experiments to evaluate the performance of the SAMS system at elevated pressures should be initiated. The parameters most important for optimal operation of the SAMS system at elevated pressures are the length of the notch filter and the magnitude of the accelerator voltage. They interact to determine the period of time that an ion spends traversing the notch filter. For successful mass rejection, it is necessary that the ions to be rejected spend time equivalent to one period of the resonance beat frequency under the influence of the notch filter field. Any increase in the accelerator voltage or decrease in notch filter length reduces the time an ion spends in the notch filter field. Therefore, these parameters must be empirically compromised to obtain the best performance. One further consideration that becomes increasingly important as the operating pressure of the separator section increases is the space charging that occurs as more and more ions are forced through the mass filter. Increasing the accelerator voltage alleviates the space charge problems but the upper limit is set by the requirement that the ion remain in the notch filter for the duration of a beat frequency. An increase in either the field radius or the operating and resonance frequencies will also decrease the space charge effects by lowering ion current density
within the notch filter. The advantages of such modifications must be weighed against the increased power requirements they entail since the power increases with the fourth power of the field radius and the fifth power of the frequency. The ion source should be modified to operate at accelerator voltages of up to two kilovolts.

Projected Analytical Applications of the SAMS Technique

The most obvious and important application of the SAMS system is for the analysis of chromatographic samples. The rejection of carrier gas ions and the subsequent analysis of gas chromatographic effluents represents an ideal application of the SAMS system. The entire packed column effluent can be utilized and only a single ion resonance field at a frequency and amplitude appropriate to reject carrier gas ions is necessary.

The analysis of liquid chromatographic effluents presents a more complex problem. Most samples analyzed by liquid chromatography are high molecular weight compounds and virtually all of the solvents employed have molecular weights less than 150. The notch filter could be operated with either one or two resonance fields so that all masses below 150 or 200 could be rejected while the heavier ions of interest would be transmitted to the analyzer mass filter for analysis. The best efforts to date for LC-MS analysis have been able to use only 1% of the effluent (Arpino, Baldwin, and McLafferty 1974). A large fraction of the LC effluent can be sent to the SAMS system because of its tolerance for high operating pressures. With proper cryobaffling and preliminary
treatment to remove the more volatile solvent prior to transfer to the vacuum system, it is possible that 100% of the sample compounds can be transferred for analysis. This preliminary desolvation could incorporate ultrasonic nebulization techniques based on the work of Denton and Swartz (1974) and Stupar and Dawson (1969).

Applications of the SAMS system to air quality monitoring and the detection of trace level environmental contaminants by direct atmospheric sampling can be readily accomplished. Removal of residual gas ions or other matrix ions can be effected using either one or two resonance fields. Subsequent analysis should be possible at trace levels below those obtained using conventional mass spectrometric methods.

In conclusion, the SAMS technique should prove to be a versatile and sensitive analytical method for the specific applications presented above and for a multitude of applications to a variety of users. In addition, the instrumentation required is technically and economically suited to development of the SAMS system as a commercially marketable package.
CHAPTER 11

STABLE ISOTOPE ANALYSIS UTILIZING PEAK AREA INTEGRATION TECHNIQUES

Introduction

The results presented in this section were obtained during the course of investigations done in conjunction with the University Analytical Center (UAC). These experiments are unrelated to the SAMS system work detailed in the previous section and were carried out using the UAC's Hewlett-Packard GC-MS-COM system.

Background

The use of stable isotopes has increased markedly in recent years because of the lower cost of enriched isotope mixtures and the mounting concern about the safety of radioactive tracers. The application of stable isotope methods to a diverse number of chemical, biochemical, and ecological problems has underscored the need for more precise mass spectrometric isotope ratio methods. Conventional isotope ratio determinations have been made by alternately sampling the appropriate peak maxima. The precision of this peak height method is ultimately determined by variations in both the peak intensity and the ability of the instrument to sample only at the peak maxima.

The quadrupole mass spectrometer is ideally suited for this type of analysis. Peak to peak switching times are of the order of a few
milliseconds (Caprioli, Fies, and Story 1974) since only the low voltage control ramp needs to be switched to change the voltages applied to the mass filter. Ion source defocusing is not a significant factor since monoenergetic ion beams are not essential because the strong focusing nature of the applied quadrupole field can tolerate these variations without noticeable performance degradation. With conventional magnetic mass analyzers, high speed switching is difficult to obtain since either large dc accelerator potential or the magnetic field strength must be switched to focus different masses at the exit slit. The former process entails ion source defocusing while the latter must overcome the time delay due to hysteresis of the applied magnetic field.

Caprioli et al. (1974) reported the use of a GC-MS-COM system for isotope ratio measurements and in the process stressed the additional problems encountered when the sample is a chromatographic effluent whose partial pressure and therefore concentration is time dependent. The relative standard deviations (RSD) were less than 1% for pure and chromatographic samples, using peak height ratios. However, they encountered problems involving the reproducibility in returning to the exact peak maxima mass locations during the rapid field switching process.

Although peak area measurements have been recognized as more precise than peak height measurements for many types of spectroscopic data, the peak area approach to mass spectrometric isotope ratio analysis has not appeared in the literature. The primary purpose of this work is to study and contrast the precision of peak height and peak
area methods for determining the isotopic ratio of analytical samples, especially gas chromatographic effluents.

**Experimental Considerations**

A Hewlett-Packard gas chromatograph-mass spectrometer-computer system consisting of a HP 5700A gas chromatograph, a HP 5930A mass spectrometer, and a HP 5932A data system was employed in these studies. Pure liquids and gases were introduced from a heated expansion volume with a variable Teflon metering valve. Gas chromatographic samples were introduced through a permselective silicon rubber membrane separator. The analyzer, ion source, and separator temperatures were maintained at 150°C for all experiments. All measurements were made using 70 eV electrons for impact ionization.

A flow diagram of the instrument control and data acquisition program is given in Figure 56. This data acquisition routine permits monitoring of any two spectral regions within the mass range of the instrument. All operator decisions are entered from the teletype keyboard during the initialization procedure. Selectable parameters include the peak scan limits, scan increment, background mass locations, and the number and duration of the samples taken at each peak. The program also provides for sampling the specified spectral regions at any multiple of 0.05 AMU. Peak maxima and integrated peak areas are calculated and stored. The sample number (inner loop) determines the length of the sampling period at each mass setting while the sweep number (outer loop) sets the number of scans through each mass spectral region. Background subtraction, peak maxima determinations, and peak area integrations are
Figure 56. Flow diagram for the experimental isotope ratio program.
performed immediately upon completion of the data acquisition. Both peak height and peak area ratios are then printed out on the teletype.

Results and Discussion

Research grade krypton and A.R. grade chlorobenzene and sulfur dioxide were analyzed using the integrated peak area technique. Preliminary characterization of the isotope ratio program was carried out using krypton introduced into the ion source by flowing the pure gas past the GC silicon rubber membrane. Krypton gas provides an excellent isotopic standard because of large number of stable krypton isotopes whose abundances are known. The six major isotopes of krypton vary in ratio from 1:1 to 162:1 and therefore provide a comprehensive test set for the evaluation of an isotope ratio technique.

Studies were performed using the $^{86}\text{Kr}$ to $^{84}\text{Kr}$ ratio to determine the effect of the experimental parameters including krypton flow rate, analyzer pressure, sample number, sweep number, and background correction on the measured precision and accuracy. Each peak was 1 AMU wide and the scan increment was .05 AMU. The variations in the height and area data are qualitatively similar. The precision and accuracy are independent of the analyzer pressure within the normal operating range ($5 \times 10^{-7}$ to $5 \times 10^{-6}$ torr). At pressures below $1 \times 10^{-7}$ torr, the precision deteriorates due to the poor ion statistics inherent in low pressure operation. The larger deviations in accuracy can be attributed to the increased effect of noise variations when background corrections are applied to less intense peaks. At pressures greater than $1 \times 10^{-5}$ torr, both precision and accuracy again begin to degrade. This may be due to
the electron impact ion source high pressure operating problems discussed previously. The extent to which this broadening affects the isotope ratio measurement is dependent upon the tuning of the electrostatic quadrupole analyzer. For example, enhancement in the sensitivity with the concurrent loss of resolution may be a viable approach when the signal strength from species of the desired mass is below optimum. However, such detuning can degrade both the precision and the accuracy if significant overlap between adjacent peaks occurs. The data presented here were obtained by tuning the instrument in the normal manner for a resolution of from two to four times the mass number throughout the instrumental mass range.

Tests conducted to determine whether the ratio measurements are affected by variations in the krypton flow rate past the membrane enricher demonstrated that precision and the accuracy are independent of the flow at flow rates greater than 2 mL/min.

Sample number (samples acquired at a mass during each scan) and sweep number (number of repetitive scans) influence both the accuracy and precision of the isotope ratio measurement. Sample numbers less than 50 frequently lead to deviations in the accuracy of the ratios and increases in the RSD's of the measurements. At sample numbers greater than 500, both accuracy and precision are degraded by long-term changes in the mass spectrometer output since the peaks being measured are no longer being sampled rapidly enough to avoid such problems. The precision of the isotope ratio measurement is relatively insensitive to sweep numbers greater than 5. This fact can be extremely useful for selecting
the measurement window around a designated chromatographic peak. Devia-
tions in the precision at sweep numbers less than five are not sur-
prising since the standard deviation is a function of the square root of
the number of trials (i.e., repetitive scans).

Applying the considerations discussed above further experiments
were conducted to measure the ratios of all the possible krypton isotope
pairings. Some representative results for both peak height and peak
area data are presented in Table 6. These measurements are the result
of 5 analyses at an analyzer pressure of $2 \times 10^{-6}$ torr. In all cases,
the peak area results exhibit better precision and accuracy than the
corresponding peak height data. This is a direct consequence of the
short-term variations in the peak maxima intensities. Figure 57 shows
the relationship between the expected isotopic ratio and the experi-
mental RSD for the peak area and peak height data of Table 1. In both
cases, the RSD's of the measurement decrease as the isotopic ratio
approaches 1. However, because of the poorer precision obtained for the
peak height results, the curve is shifted to higher values. The peak
area RSD's are a factor of from two to four better than the corresponding
peak height RSD's. The superiority of the peak area technique increases
markedly with increasing isotopic ratio. This inverse relationship
between the RSD and the isotopic ratio has been reported in a previous
isotopic ratio study utilizing quadrupole mass spectrometers. This
study utilized the peak height method and the results reported were
comparable to the peak height data obtained in this work.
Table 6. Isotope ratio data for isotopes of krypton.

<table>
<thead>
<tr>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Ratio</th>
<th>RSD (%)</th>
<th>Deviation of mean (%)</th>
<th>Ratio</th>
<th>RSD (%)</th>
<th>Deviation of mean (%)</th>
<th>Expected value</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>84</td>
<td>161.6</td>
<td>0.3094</td>
<td>-0.600</td>
<td>157.8</td>
<td>1.0869</td>
<td>-2.95</td>
<td>162.57</td>
</tr>
<tr>
<td>78</td>
<td>86</td>
<td>49.59</td>
<td>0.2339</td>
<td>-0.086</td>
<td>47.88</td>
<td>0.5521</td>
<td>-3.52</td>
<td>49.63</td>
</tr>
<tr>
<td>78</td>
<td>82</td>
<td>33.06</td>
<td>0.2228</td>
<td>0.098</td>
<td>32.84</td>
<td>0.6846</td>
<td>-0.559</td>
<td>33.00</td>
</tr>
<tr>
<td>80</td>
<td>84</td>
<td>24.76</td>
<td>0.1629</td>
<td>-1.23</td>
<td>24.56</td>
<td>0.4528</td>
<td>-2.03</td>
<td>25.07</td>
</tr>
<tr>
<td>80</td>
<td>86</td>
<td>7.420</td>
<td>0.0702</td>
<td>-3.01</td>
<td>7.304</td>
<td>0.2521</td>
<td>-4.53</td>
<td>7.65</td>
</tr>
<tr>
<td>82</td>
<td>84</td>
<td>4.904</td>
<td>0.0840</td>
<td>-0.326</td>
<td>4.877</td>
<td>0.3356</td>
<td>-0.868</td>
<td>4.92</td>
</tr>
<tr>
<td>83</td>
<td>86</td>
<td>1.466</td>
<td>0.1088</td>
<td>-2.28</td>
<td>1.462</td>
<td>0.2270</td>
<td>-2.52</td>
<td>1.50</td>
</tr>
<tr>
<td>84</td>
<td>86</td>
<td>3.418</td>
<td>0.0681</td>
<td>+4.24</td>
<td>3.448</td>
<td>0.1730</td>
<td>+5.15</td>
<td>3.279</td>
</tr>
</tbody>
</table>
Figure 57. Graphical comparison of the precision for the peak area and peak height techniques using krypton as the sample.
Additional investigations were carried out using chlorobenzene which was allowed to leak into the ion source from the HEV to a constant analyzer pressure of \(3 \times 10^{-6}\) torr. The \(^{37}\)Cl to \(^{35}\)Cl ratio was evaluated by monitoring the molecular ions at m/e 114 and 112 and the data are presented in Table 7. Five repetitive analyses were run and a relative standard deviation of less than 0.08% was achieved.

A third study was performed to determine the \(^{32}\)S to \(^{34}\)S ratio in pure \(\text{SO}_2\) by monitoring the molecular ions at m/e 64 and 66. Sulfur dioxide was introduced into the ion source to a constant analyzer pressure of \(6 \times 10^{-6}\) torr from the HEV. The results, also presented in Table 7, show an RSD of approximately 0.05% for five consecutive trials. The results in parentheses are the experimental values theoretically corrected for the \(^{18}\)O contribution m/e 66 peak.

Gas Chromatographic Samples

To be of greatest general analytical significance, it is desirable that an isotope ratio method be able to give precise results for GC effluents. Chromatographed samples present a twofold problem: 1) the total sample involved is usually small; and 2) during the elution of the peak the sample concentration is rapidly varying, requiring that the sampling routine employed be versatile enough to deal with these limitations without significant loss of precision.

Both chlorobenzene and sulfur dioxide were analyzed chromatographically. Chlorobenzene was chromatographed on a 6 ft x 1/4 in. column packed with 10% UCON on Chromosorb W. Sample standards were run using both benzene and methanol as solvents. One microliter injections
Table 7. Isotope ratio data for heated expansion volume and chromatographic samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Introduction mode</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Sample/Sweep</th>
<th>Peak area ratio</th>
<th>Peak area RSD (%)</th>
<th>Peak area deviation of mean (%)</th>
<th>Expected value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>pure</td>
<td>114</td>
<td>112</td>
<td>100/100</td>
<td>0.3221</td>
<td>0.0758</td>
<td>-0.587</td>
<td>0.3240</td>
</tr>
<tr>
<td>$^{37}$Cl/$^{35}$Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>GC methanol</td>
<td>114</td>
<td>112</td>
<td>100/100</td>
<td>0.3244</td>
<td>0.1190</td>
<td>0.124</td>
<td>0.3240</td>
</tr>
<tr>
<td>$^{37}$Cl/$^{35}$Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>GC benzene</td>
<td>114</td>
<td>112</td>
<td>100/100</td>
<td>0.3196</td>
<td>0.1080</td>
<td>-1.33</td>
<td>0.3240</td>
</tr>
<tr>
<td>$^{37}$Cl/$^{35}$Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{34}$S/$^{32}$S</td>
<td>pure</td>
<td>66</td>
<td>64</td>
<td>100/10</td>
<td>(0.04406)*</td>
<td>0.0503</td>
<td>-0.675</td>
<td>0.0444</td>
</tr>
<tr>
<td>$^{34}$S/$^{32}$S</td>
<td>GC</td>
<td>66</td>
<td>64</td>
<td>100/100</td>
<td>(0.04443)*</td>
<td>0.0657</td>
<td>0</td>
<td>0.0444</td>
</tr>
</tbody>
</table>

*Ratios corrected for $^{18}$O contribution in parentheses.
(1 μg μL⁻¹ chlorobenzene) were used in each case. The results which appear in Table 7 show that the relative standard deviations of approximately 0.1% were observed. The solvents chosen for the GC analyses demonstrate the ability of the peak area algorithm to deal with unresolved chromatographic peaks. In the benzene system, the chlorobenzene peak is resolved to the baseline while considerable peak overlap occurs in the methanol system. However, the precision of the ratio measurement is virtually identical for the two chromatographic systems. Chromatographic peak overlap is therefore shown not to be a problem provided that the peaks monitored are not common to both compounds.

Further chromatographic studies were performed using SO₂. The analysis was performed using a 3 ft by 1/4 in. column packed with 2% SE 30 on Chromosorb W. The results given in Table 3 demonstrate precisions on the order of 0.07% were obtained.

Conclusions

These investigations demonstrate the improved precision of isotope ratio measurements using integrated peak areas rather than peak height intensities. In all experiments, the peak area data are found to be more precise than the peak height data and less sensitive to changes in instrumental tuning. Relative standard deviations were enhanced by a factor of from two to four for isotope ratios of 1:1 to 162:1. The improved precisions are possible because difficulties arising from the variable intensities and mass locations of the peak maxima during analysis are circumvented by the peak area technique. Relative standard
deviations varying between 0.05 and 0.3% are observed and gas chromatographic samples can be readily analyzed.

These studies were carried out using a commercial instrument with no additional hardware modifications or instrumental detuning and can be easily implemented by other investigators since the integrated peak area approach is readily adaptable to other computer-controlled quadrupole GC-MS systems.

In addition to the pure and chromatographed samples analyzed here, the peak area method should also be useful for the analyses of mixtures using either mass fragmentography or one of the recently developed "soft" ionization techniques such as chemical ionization (Munson 1971), field ionization (Anbar and Aberth 1974), field desorption (Beckey 1969), or atmospheric pressure ionization (Carroll et al. 1974).
VACUUM SYSTEM PUMPDOWN, SHUTDOWN, AND VENTING PROCEDURES

Vacuum System Pumpdown

1. Close sample, vent, foreline, and roughing valves.
2. Turn on the rough pump.
3. Slowly open foreline valve and allow the system to be slowly roughed.
4. If gate valve is closed, open the roughing valve to rough the vacuum chamber. After roughing the vacuum chamber, open gate valve and close roughing valve.
5. When the thermocouple gauge reads approximately zero microns, turn on the coolant water to the diffusion pump.
6. Turn on the diffusion pump.
7. Allow 30 minutes for residual system pressure to be reached. If the system or any components have been opened to the atmosphere for a long period of time, residual system pressure will be reached more slowly.
8. Turn on Bayard-Alpert Ionization gauge, check the calibrate and record system pressure.
9. The system is now ready for operation.
Vacuum System Shutdown

1. Turn off the Bayard-Alpert Ionization gauge.
2. Turn off the diffusion pump. Only the foreline valve should be open at this point.
3. Turn on the water flow through the quick-cool lines. This allows the diffusion pump oil heater to cool more rapidly.
4. Allow approximately 1 hour then lightly touch the bottom of the diffusion pump. If it is cool or slightly warm, go on to step 5; if not, allow more cooling time.
5. When the diffusion pump is cool, close the foreline valve.
6. Allow the vacuum system to remain under vacuum or fill it with dry nitrogen through the vent valve.
7. Turn off the thermocouple vacuum gauge.
8. Turn off the diffusion pump and quick-cool water.
9. Blow out the quick-cool line with compressed air. This will minimize hot water corrosion effects during the next operating cycle.

Vacuum Chamber Venting without Diffusion Pump Shutdown

1. Close the gate valve.
2. Use vent valve to bring vacuum chamber to atmospheric pressure.
3. Access to the vacuum chamber is now possible.
4. To initiate the vacuum chamber pumpdown procedure, close the foreline valve to stall the diffusion pump. Never stall the diffusion pump for more than 5 minutes.
5. With diffusion pump stalled, open the roughing valve and rough the vacuum chamber until the thermocouple gauge reads below 50 microns.

6. Close the roughing valve.

7. Open the foreline valve.

8. Open the gate valve. If the roughing valve is open during this step, oil vapor from the stalled diffusion pump will be brought into the vacuum chamber region.

9. Allow 10 minutes for the system to reach residual pressure.

10. The system is now ready for operation.
APPENDIX B

CRITICAL DIMENSIONS FOR ELECTRODE DISTANCES

<table>
<thead>
<tr>
<th>Rod diameter (in.)</th>
<th>$r_o$ (in.)</th>
<th>$d_{cr}$ (in.)</th>
<th>$d_{rr}$ (in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4</td>
<td>.1089</td>
<td>0.2339</td>
<td>0.4678</td>
</tr>
<tr>
<td>3/8</td>
<td>.1633</td>
<td>0.3508</td>
<td>0.7016</td>
</tr>
<tr>
<td>1/2</td>
<td>.2178</td>
<td>0.4678</td>
<td>0.9356</td>
</tr>
<tr>
<td>5/8</td>
<td>.2722</td>
<td>0.5847</td>
<td>1.1694</td>
</tr>
<tr>
<td>3/4</td>
<td>.3266</td>
<td>0.7016</td>
<td>1.4032</td>
</tr>
<tr>
<td>7/8</td>
<td>.3811</td>
<td>0.8186</td>
<td>1.6372</td>
</tr>
<tr>
<td>1</td>
<td>.4355</td>
<td>0.9355</td>
<td>1.8710</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

a  Mathieu equation parameter characteristic of the applied dc potential

a' dimensionless constant representative of the space charge effect expressed in terms of a perturbation to the dc potential

e  charge of an electron

f  frequency of the applied ac potential

\( f_{nf} \)  notch filter quadrupole field frequency

\( f_{res} \)  notch filter homogeneous resonance field frequency

k  constant equal to \( 4eE'/Mw^2 \)

l  length of the quadrupole filter

m  ion mass

n  number of ac field cycles

q  Mathieu equation parameter characteristic of the applied ac potential

r  quadrupole electrode radius

\( r_o \)  quadrupole field radius

s  any integer

t  time in seconds

u  positional parameter used to represent \( x \) or \( y \)

\( u_o \)  initial position of an ion injected into the quadrupole field
\( v_z \) ion injection energy

\( x \) Cartesian positional coordinate

\( y \) Cartesian positional coordinate

\( z \) Cartesian positional coordinate

\( C \) constant dependent solely on the operating point \((a,q)\)

\( E \) electrical potential at any point \((x,y,z)\) within the applied field

\( E_0 \) position independent factor characteristic of the applied potential waveform

\( E' \) the homogeneous resonance field

\( I \) ion current

\( I_d \) dark current

\( I_e \) ion source emission current

\( L \) inductance

\( M \) ion mass in atomic mass units

\( M_{\text{res}} \) resonance mass in atomic mass units

\( P \) pressure

\( R \) resolution

\( S, S' \) fundamental solutions to the homogeneous Mathieu equation

\( S_{\text{res}} \) resonance solution

\( U \) applied dc potential between electrode sets

\( V \) one-half of the applied peak to peak ac potential between electrode sets

\( V_{nf} \) notch filter ac quadrupole field voltage amplitude (zero to peak)
$V_{res}$ resonance field voltage amplitude (peak to peak)
$W$ Wronskian determinant.
$\alpha$ constant of integration
$\beta$ parameter characteristic of the frequency of ion motion
$\gamma$ weighting factor for the $z$ positional coordinate
$\lambda$ weighting factor for the $x$ positional coordinate
$\mu$ constant dependent only on the operating point $(a,q)$
$\xi$ time, defined as $\omega t/2$
$\sigma$ weighting factor for the $y$ positional coordinate
$\omega$ angular frequency of the applied ac field
$\omega'$ angular frequency of the applied resonance field
$\Delta$ Laplacian operator
$\phi$ applied potential
$\phi_0$ potential between opposite electrode pairs
REFERENCES


Aston, F. W., Phil. Mag., 38, 707 (1919).


Berkling, K., Diplomarbeit, University of Bonn, 1956.


Mclachlan, N. W., Theory and Application of Mathieu Functions, Oxford University Press, New York, 1951.


