THE THREE DIMENSIONAL QUADRUPOLE MASS SPECTROMETER

by

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SUMMARY

A new type of mass analyzer has been studied with a view to increasing discrimination and sensitivity capabilities. The three dimensional quadrupole mass spectrometer may be used as a universal trace gas analyzer or in the ion gauge mode as an ultra-high vacuum gauge. The instrument is capable of storing a specific mass-to-charge ratio or a range of such ratios for a sufficient time accumulating the species until they become detectable. The instrument was built and tested for practicality of operation, reliability and sensitivity.

Results indicated that there are several areas of uncertainty in the operation of the instrument. The most significant of these were the ionization and detection processes. Otherwise, the instrument demonstrated its most useful capability of trapping and accumulating a species. This is seen as a significant step in the process of attaining higher degrees of sensitivity in trace gas analyzers.
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$\Delta m$:

1. **Experimental**: The width of a peak at half-height in mass units.
2. **Theoretical**: The length of a scan line inside a stability region in mass units.
1. INTRODUCTION

The electrodynamic suspension of charged particles of a specific mass to charge ratio was first reported by Wuerker, Shelton, and Langmuir in 1955. Charged particles of the order of microns in size were trapped, and their trajectories were recorded by microphotography. Since then, such an instrument has assumed increasing importance in the field of mass analysis. Because of its ability to suspend and therefore store a specific mass to charge ratio, the instrument shows promise of having much higher limits of sensitivity than conventional mass analyzers. Unfortunately, this advantage has not yet been fully realized, due to the many problems which still plague the three dimensional quadrupole.

In 1967, P. H. Dawson and N. R. Whetten published a series of papers on the three dimensional quadrupole. More recently, Dawson now at Laval University has continued his research in this topic. As well, C. S. Harden and P. E. Wagner are also carrying on similar research under the auspices of the United States Defence Department. Much of the above work will be used in this report for the purpose of comparison.

As mentioned in the summary, the instrument has the potential of becoming a very high sensitivity trace-gas analyzer; however, the long-term goal of this project is with a view to operating it as a fly-through molecular beam detector. This was envisaged as a system in which a molecular beam would be continually ionized by an electron beam running in a direction perpendicular to the molecular beam.

2. BASIC OPERATION

The three dimensional quadrupole is an electrode consisting of a ring (or short cylinder) and two end-caps (see Fig. 1). The internal surface of the ring electrode is shaped into a hyperbola of revolution, while that of each of the end-caps is machined into a hyperbola of rotation. The two hyperbolas are complimentary so that their asymptotic cones are coincident.

If the proper combination of RF and DC voltages is applied between the end-caps and the ring electrode, charged particles of a specific mass to charge ratio will be caused to follow a closed trajectory within the chamber. One important criterion for these charged particles is that they must enter the chamber as neutrals. To facilitate this, an orifice is drilled at a convenient point through the chamber to allow an electron beam to enter and ionize the neutral particles within the closed system. Sufficient room is allowed between the end-caps and the ring electrode to permit neutrals to diffuse into the chamber.

After the ions have been stored, they must be detected. To accomplish this, an additional voltage is applied periodically (withdrawal pulse) between the end-caps to deflect the stored ions toward one of the end-caps which is perforated to allow the ions to leave the chamber and enter the detection device. To ensure that only the stable "m/e" ratios are detected, there can be no ionization occurring during the withdrawal pulse; as well, ionization must be terminated, for a sufficient period prior to withdrawal, to allow all unstable mass to charge ratios to be
lost to the electrodes. For this purpose, a control electrode is placed between the electron-emitting filament and the chamber orifice. The electron accelerating voltage is obtained from the potential of the ring electrode, so that electrons enter the chamber only during those portions of the RF cycle in which the potential of the ring is positive. In addition, a negative potential is applied at the control electrode in the form of a pulse (control pulse) so as to prevent the entrance of electrons into the trap during the peak of the positive RF voltage.

Both the control pulse and the withdrawal pulse are triggered by the same device which has a delay feature. This makes control of both pulses possible so that the electron beam is effectively shut-off for a specific period prior to and during the detection process. Figure 2 depicts the pulsing procedure.

The withdrawn ions are detected using a 15 stage windowless photomultiplier. The multiplier is well encased inside a magnetic shield as well as an additional ground shield. From the anode, the multiplied signal is amplified by a high input-impedance operational preamplifier and then by an AC amplifier. The signal is then peak rectified and fed into an x-y recorder. Detailed diagrams of the amplification circuitry are shown in Figures 3 and 4.

3. THEORETICAL BACKGROUND

3.1 Determination of the Necessary Electric Fields

For a particle motion to be confined within a closed region, the force generated by an electric field must have a radial component that is directed inward and increases in magnitude with distance from the center of the chamber. If this is to apply to all directions from the center of the chamber, the electric potential must be an even function of the coordinates "x, y, z". Because of the geometry of the chamber it is convenient to use, in this case, cylindrical coordinates. Let

\[ \Phi(r, z) = \Phi_0(\alpha r^2 + \gamma z^2) \]  

(1)

(where the x-y plane containing "r" is that plane perpendicular to the axis of the ring).

The total charge inside the chamber may be neglected with respect to charge density. Therefore, we may apply Laplace's equation:

\[ \nabla^2 \Phi = 0 \]  

(1a)

but from (1)

\[ \nabla^2 \Phi = \Phi_0 \left\{ \alpha(4) + 2\gamma \right\} \]  

(2)

from (1) and (1a)

\[ \alpha = -2\alpha \]  

(3)

\[ \gamma = -2\alpha \]

(4)
\[ \alpha = \frac{1}{2} r_o^2 \]  

Also
\[ \phi \bigg|_{r=0} = -\phi /2 = -\phi \bigg( \frac{2z_o^2}{z = z_o} \bigg) \]
\[ \alpha = \frac{1}{4} z_o^2 \]  
\[ r_o^2 = 2z_o^2 \]  

(\text{where: } r_o \text{ and } z_o \text{ represent the minimum distance of the appropriate hyperbola to the origin}).

Equation (7) fixes the dimensions of the chamber. The potential at any point inside the chamber is then:
\[ \phi = \phi_o \frac{1}{4z_o^2} (r^2 - 2z^2) \]  

(8)

As has already been mentioned the applied potential is a combination of RF and DC potentials. If \( \omega \) represents the RF frequency, let us write this potential as:
\[ \phi_o = U_{dc} - V_{ac} \cos (\omega t) \]  

(9)

From (8) and (9)
\[ \phi(r,z) = \left( U_{dc} - V_{ac} \cos(\omega t) \right) \left( \frac{1}{4z_o^2} \right) \left( r^2 - 2z^2 \right) \]  

(10)

3.2 Transformation into the Mathieu Equation

The electric fields in the "z" and "r" directions are independent. Therefore, in component form we have:
\[ E_r = \frac{3\phi}{3r} = - \frac{r}{2z_o^2} \left( U_{dc} - V_{ac} \cos(\omega t) \right) \]  

(11)
\[ E_z = \frac{3\phi}{3z} = \frac{z}{z_o^2} \left( U_{dc} - V_{ac} \cos(\omega t) \right) \]  

(12)

The equations of motion in each of the directions may then be written:
\[ \frac{d^2r}{dt^2} + \frac{e}{m} \left( \frac{r}{2z_o^2} \right) \left( U_{dc} - V_{ac} \cos(\omega t) \right) = 0 \]  

(13)
\[
\frac{d^2z}{dt^2} - \frac{e}{m} \left( \frac{z}{z_o} \right) \left( U_{dc} - V_{ac} \cos(\omega t) \right) = 0
\] (14)

And if for (14) we let
\[
\begin{align*}
    a_r &= 2 \left( \frac{e}{m} \right) \left( \frac{U_{dc}}{z_o \omega} \right) \\
    q_r &= \left( \frac{e}{m} \right) \left( \frac{V_{ac}}{z_o \omega} \right)
\end{align*}
\]

\[
\omega t = 2\xi
\]

So that:
\[
\frac{d^2r}{d\xi^2} + (a_r - 2q_r \cos 2\xi) r = 0
\] (16)

Similarly, we arrive at an equation of the same form for the \( z \)-component from which we obtain the following relationships:
\[
\begin{align*}
    a_z &= -2a_r \\
    q_z &= -2q_r
\end{align*}
\] (17)

Equation (16) has the form of the Mathieu Equation. From this it is evident that if the alternating force (2q) vanishes, the ions will oscillate with a natural frequency of \( \sqrt{a_r} \) and \( \sqrt{a_z} \) in the respective directions.

3.3 Stability Criteria

The general solution to the Mathieu Equation may be written as:
\[
u = a e^{\mu \xi} \sum_{s=-\infty}^{\infty} C_{2s} e^{2is\xi} + a e^{-\mu \xi} \sum_{s=-\infty}^{\infty} C_{2s} e^{-2is\xi}
\] (18)

(where "\( u \)" represents either "\( r \)" or "\( z \)").

Equation (18) has two types of solutions as \( \xi \to \infty \):

(i) "\( u \)" \( \to \infty \)

(ii) "\( u \)" remains finite.

It is obvious that for a closed path, the latter solution applies. Such a condition will exist, if and only if \( \mu = i\beta \); where "\( \beta \)" is a non-integer constant. In this case we may write:
\[ u = \alpha_1 \sum_{s = -\infty}^{\infty} C_{2s} \cos(2s + \beta) \xi + \alpha_2 \sum_{s = -\infty}^{\infty} C_{2s} \sin(2s + \beta) \xi \quad (19) \]

If we let the fundamental frequency of the ion be \( \Omega \) then:

\[ \beta \xi = \Omega t \quad (20) \]

Also from (15) and (20) we have:

\[ \frac{\beta}{2} = \frac{\Omega}{2} \quad (21) \]

Equation (21) defines the non-integer constant of the bounded solution (i.e., Equation (19)) in terms of the fundamental frequency of the trapped species and the applied RF frequency.

It has been shown (11) that for a specific \( \beta \) value there is a definite relationship between the parameters \( a \) and \( q \) defined in Equation (15). Furthermore, the most interesting points in an \((a,q)\) diagram which provide bounded ion motion are those between the \( \beta = 0 \) and \( \beta = 1 \) curves*. For example, for stability in the \( r \)-direction, the two relationships are:

\[ a_r = -\frac{1}{2} q_r^2 + \frac{1}{128} q_r^4 - \frac{29}{2304} q_r^6 + \frac{6867}{18874368} q_r^8 \quad \text{for} \quad \beta = 0 \quad (22) \]

\[ a_r = 1 - q_r - \frac{1}{8} q_r^2 + \frac{1}{64} q_r^3 - \frac{1}{1536} q_r^4 - \frac{11}{3584} q_r^5 \quad \text{for} \quad \beta = 1 \quad (23) \]

Similar equations may be obtained for the \( z \)-direction, through use of the transformation equations (17).

These curves were plotted for this investigation and the "\( r \)" and "\( z \)" stability diagrams superimposed to produce a 3-dimensional stability diagram. (see Fig. 5)**. This plot will be recognized as being very similar to the 2-dimensional stability diagram of a conventional quadrupole mass filter, with the exception of the asymmetry about the \( q \)-axis. From this point on, the theory is very similar to a 2-dimensional quadrupole filter. For example, any point on the \((a,q)\) diagram represents a specific mass to charge ratio. If this point lies inside the stability region the mass is stable.

From (15), if the ratio \( e/m_0^2 \Omega^2 \) is kept constant while \( V_{ac} \) is varied, the "\( q \)" varies proportionately and we have a means of mass scanning. If the ratio \( V_{ac}/Udc \) is also kept constant during the procedure, then we are mass scanning along a straight line (i.e., scan line) with constant slope in the \((a,q)\) diagram, passing through the origin.

* There are other regions of the \((a,q)\) plane where a mass is stable in both the "\( r \)" and "\( z \)" directions; however, these other regions are much smaller and require much higher voltages. To this date, no one has attempted to study them experimentally.

** Figure 5 was obtained through the Computer facilities at UTIAS.
3.4 Theoretical Resolution

Now that we have developed a theoretical procedure for differentiating between stable and unstable masses, it becomes a simple matter to define "theoretical resolution". (For relation to experimental resolution see Section 5.2). Such a resolution must be related to the proportion of the scan line inside the stability region to that outside of it. It is evident that this ratio is related to the slope of the scan line which is in turn controlled by the "Vac/Udc" ratio. For example, if the scan line slope is zero, all masses from "q = 0" to "q = 0.92" will be stable, and the analyzer will be operating in an ion-gauge mode. As the magnitude of the slope increases, the resolution increases until the scan line crosses the intersection of the \( \beta_r = 1 \) and \( \beta_z = 0 \) lines (i.e., the tip of the stability diagram).

IV. EXPERIMENTAL SET-UP

The three-dimensional quadrupole was machined from 304 stainless steel. Each of the end-caps was built in two parts; a part containing the hyperbolic surface, and a flange. Both pieces were threaded so that the end-caps could be moved in a direction perpendicular to the plane of the flanges. A diagram of the instrument is given in Figure 6.

The ionizing electron beam was produced from an incandescent 0.010" diameter tungsten filament, accelerated by the electric field between the filament and the ring electrode and directed into the chamber through an entrance aperture in the ring electrode. The power for the filament was taken from a Kepco DC Regulated Power Supply.* The filament potential was varied by direct connection to the negative output of a 300 volt NVE Model S-400 DC Power Supply. Entrance of the electron beam into the chamber could be terminated by a negative pulse (control pulse) applied to the control electrode from a Servo 2100 Series Pulse Generator.

An Extranuclear Model 169 Quadrupole Power Supply (QPS) was used to provide the required RF and DC fields for the ion-trap. This particular power supply was built for a conventional 2-dimensional mass filter, and is therefore a two-ended device providing potentials of \((1/2)(\text{Vac-Udc})\) for one end, and \(-(1/2)(\text{Vac-Udc})\) for the other. This device was used in an one-ended mode with the full power being applied to the ring electrode. The upper end-cap was electrically grounded, while the lower was connected to the delayed positive output of the Pulse Generator mentioned above. This pulse (withdrawal pulse) could be delayed between 1 to 10,000 microseconds after the control pulse was initiated. This positive pulse would deflect the trapped ions toward the upper end-cap which was perforated to allow them to enter the detection device.

Because the quadrupole power supply was built for a 2-dimensional mass filter, the maximum "DC/AC" ratio obtainable was much below the optimum required for the 3-dimensional ion-trap. The latter requirement is a ratio of just over 1/4 while the ratio needed for the mass filter is only about 1/6. To achieve this higher ratio, some of the circuitry of the High-Q Head

* Initially, an AC current supply was used; however, it was found that this created unwanted emission current fluctuations at 120 Hz which appeared at the multiplier output. This is believed to be due to a full-wave rectification effect, since the emission current peaks twice during each AC cycle.
had to be altered. The latter is the output device for the QPS which accomplishes the mixing of the high AC and DC voltages. Unfortunately, this modification lowered the upper voltage limit attainable by the QPS.

As a result of the proximity of the control electrode and the lower end-cap to the very high RF voltages of the ring electrode, a problem developed due to induced RF potentials being dissipated across the matching resistor of the Pulse Generator. To overcome this problem, capacitors were placed in the circuitry to drop the induced RF to ground while allowing the pulse signal to arrive at the end-cap and the control electrode. It was necessary to use high voltage rating capacitors (1 kV) to ensure against breakdown from the high induced voltages.

The first stage in the detection circuitry was an EMI BeCu Oxide coated 15-stage Electron Multiplier. Prior to entering the multiplier, the ions passed through a grounded copper wire mesh which was isolated by an additional wire mesh grounded cylinder, in order to reduce the RF pick-up at the multiplier. Inside this was placed a magnetic shield which not only protected the multiplier from the magnetic field fluctuations but also picked up stray ions by virtue of the fact that it was kept at the potential of the first dynode (-2.5 kV). Near the first dynode of the multiplier was a small tungsten filament used to measure the gain of the multiplier. The emission current of the filament was measured and compared to the output current of the multiplier, and a gain factor was obtained of approximately $10^4$ at 2.5 kV. The quoted gain of the multiplier had been $6.6 \times 10^4$ at 2.5 kV; however, the manufacturer had warned that prolonged exposure to atmospheric conditions deteriorated the efficiency of the multiplier, although this deterioration levelled off at about a gain of $10^4$. The initial work with the equipment involved considerable exposure of the multiplier to the atmosphere, and this would explain the deterioration observed.

The output signal from the multiplier was in the form of short pulses (less than 10 microseconds long) superimposed on a small DC signal (i.e., although minimized, there was still a trace of continuous flow of stray ions into the multiplier, appearing as a DC signal) and RF pick-up. A photograph of the multiplier output is shown in figure 7. The peak to peak value of the RF pick-up was of the order of the pulsed signal at $m/e = 28$. An appropriate capacitor was used to drop most of the RF (1.25 MHz) to ground while allowing the output signal (approx. 1 KHz) to pass. The solution however, was not as simple with regard to removal of the DC signal. The output signal, for instance, could not be amplified by a high impedance operational amplifier because of the latter's discrimination against higher frequencies. That is to say, an operational amplifier has maximum gain for a DC signal, with the gain dropping-off with increasing frequency. This meant that with any reasonable amplification factor there would be a drastic distortion of the signal with the major part of the output being DC.

The alternative of using a wide band AC amplifier was not much more encouraging because all such readily available amplifiers contained 50 ohm matching input and output impedances. Since the output signal of the multiplier was of the order of one microamperes, the potential difference created across the 50 ohms would be a mere 50 microvolts. This signal was much too small to be seen by any of our available AC amplifiers. What was needed was a high input impedance amplifier that was not overly partial to DC.
The compromise arrived at, was to use a low-gain, wide-band, high input impedance operational preamplifier followed by a wide-band AC amplifier.* The operational amplifier boosted the signal sufficiently to be seen by the AC amplifier. A coupling capacitor was placed between the two instruments to prevent DC developed at the preamplifier stage from entering the AC amplifier. After this stage, the signal was passed through a positive peak rectifier with an RC constant of 3.0 seconds and then fed into an x-y recorder.

In the hope that the ionization current inside the trap could be measured directly, an orifice was drilled into the ring electrode diametrically opposed to the electron beam entrance and a Faraday cup was placed directly behind it. However, due to the highly divergent paths of the electrons inside the chamber, it was impossible to interpret current readings obtained at the Faraday cup in terms of the ionization current near the center of the trap. It is this current, near the center of the chamber which produces candidate ions for trapping. This arises from the fact that the amplitude of oscillation for the ions increases with distance from the center of the chamber. The ions will therefore be lost when their amplitude is such that they hit the walls of the chamber. (i.e., when they are formed too far from the center of the chamber).** In the emission measurements which were made, a Keithley 640 Electrometer was connected to the ring electrode, with the RF power source turned off. The potential difference between the filament and the ring electrode was kept at some value representing the average potential which the electrons would see if the RF source were on. Since the resulting emission current reading obtained represented all the electrons reaching the ring electrode (i.e., and not only those going through the center of the trap), it could only be taken as an upper limit indication of the "effective" ionization current.***

V. EXPERIMENTAL RESULTS

5.1 Identification of Mass Spectrum

Various gases were dried by passing them through a cold trap held at the appropriate temperature to freeze out any residual water vapour, and leaked into the main vacuum chamber. The chamber base pressure was $2 \times 10^{-8}$ torr. The gases used were Helium, Oxygen, Nitrogen, and carbon dioxide. Of these gases, the most revealing by far was carbon dioxide. With carbon dioxide as the leak gas, 11 mass peaks were identified, from $m/e = 12$ to $m/e = 44$, as shown in figure 8a. Figure 9 shows mass peaks 14 to 18 in greater detail. The significant presence of the $m/e = 16$ peak is expected due to a contribution from the $O^+$ from carbon dioxide. The water peaks (i.e., $m/e = 18, 17$ and 16) are evidence of the fact that water vapour had remained adsorbed onto the glass walls of the vacuum chamber. When $O_2$ was leaked into the system $m/e = 32$ became by far the dominant peak.

The filament emission current was kept at a very low level of the order of one microampere. Throughout these runs only a small fraction of this total emission current is actually effective in producing ions capable of being trapped in the ionization process. The reason for this has already

* Figure 4 contains a detailed diagram of the amplification circuitry.
** This phenomenon results in an interesting advantage when a well collimated molecular beam is to be studied.
*** "Effective" ionization current is that portion of the electron current which produces ions capable of being trapped.
been pointed out in terms of the diverging electron paths inside the chamber.

An ion withdrawal pulse of 40 volts was applied at a frequency of 800 Hz for a duration of 4 to 6 microseconds. The withdrawal pulse was preceded by 20 microseconds by a negative control pulse (i.e., applied to the control electrode) of 30 microseconds duration. Since the RF frequency was set at 1.25 MHz, this procedure allowed ions to be stored for 1500 RF cycles (i.e., 1.22 msec) and prevented ionization (i.e., while also allowing all unstable ions to be lost to the walls of the chamber) for a period of 25 RF cycles, at which point, the trapped ions were collected for 5 to 8 RF cycles. With regard to the 40 volt withdrawal pulse duration, the peak height increased rapidly for the values below 3 microseconds, only slightly between 3 and 6 microseconds, and not at all beyond six.

5.2 Resolution Studies

The two principal mass peaks observed in the background gas, at pressures ranging from 10^-6 to 10^-8 torr, were \( m/e = 18 \) and \( m/e = 28 \). Peak shape studies with varying resolution were made for these species for comparison with the data obtained from the work of Dawson and Whetten. Figure 10 contains the results for \( m/e = 28 \).

In the course of these experiments it was found that resolution was not the only parameter affecting peak shape. Variations in filament emission and (or) background pressure resulted in distortion of the peak shapes. Generally, it was found that the minimum ionization current for a specific pressure gave the best peak shape. It would seem that an increase in ion density in the trap has a space charge effect which indirectly results in a change in peak shape. The space charge problem is considered in greater detail later in this report.

With a sufficiently low filament emission current, peak shapes were obtained which were very similar to those by Dawson and Whetten. As was expected peak splitting vanished as maximum resolution was approached. This is a phenomenon common to most mass spectrometers. A maximum resolution (i.e., \( m/\Delta m \)) of over 200 was achieved for \( m/e = 28 \).*

From figure 10 it is evident that with an increase in resolution, the lower mass side of the peak moved inward faster than the higher mass side. This characteristic was also found for the \( 44 \) peak of CO. The explanation for this phenomenon arises from a consideration of the shape of the stability region and will also be discussed in detail later in this report.

With regard to the actual peak shapes, low resolution modes are characterized by considerable peak-splitting, as shown in figure 11. The first photograph in which \( m/\Delta m = 10 \) shows 6 peaks characterizing the \( m/e = 28 \) peak. The third photograph, however, shows that with a resolution of 30 the base width has decreased, and the shape has changed drastically into a single clear peak.**

In the aforementioned photographs the filament was kept at ground potential. An interesting phenomenon was observed when this potential was varied.*** When the filament potential was kept at a negative value (e.g. * With regard to experimental results "\( \Delta m \)" represents the mass width of the peak at half-height in mass units.
** The vertical sensitivities for each of these photographs were not kept the same.
*** See figure 12.
- 40 v), the peak heights were much greater and higher resolution modes could be attained. For this data the filament emission was kept at a very low level. The increase in ionization current resulting from an increase in the (negative) filament potential (ie, increasing the electron accelerating potential) probably explains the increase in peak height. Reasons for the variation in peak shape are not as clear, although there is an indication that the space charge effect already mentioned may be involved. Another effect which may be significant in this case is one relating to the RF phase at the instant of ionization. Such an effect has been reported by both Dawson and Harden\(^{(2,9)}\).

Another observation in this series of experiments relates to the relative resolution of various mass peaks. Prior to discussing this however, it may be useful to relate the theoretical resolution obtainable from a stability diagram to an experimental one as obtained from mass spectra. The latter has already been described as being the ratio of the mass number at the center of a resolved peak to the width of that peak at half-height in mass units. Although not as well defined, the theoretical resolution relates the length of the scan line to that portion of the scan line within the stability region. A convenient definition for the upper end of the scan line is the intersection of the scan line and a line drawn parallel to the "a" axis passing through the tip of the stability diagram. The convenience of such a definition should become more apparent in the discussion of "peak shifts".

If the scan line passes through the tip of the stability region, then the mass number being studied is linearly proportional to the length of the scan line*. Therefore, if a certain fraction of the scan line were within the stable region, then that same fraction of mass numbers would also be stable and appear as a single peak on the x-y recorder. Hence, the ratio of the scan line length to that portion within the stability region is equivalent to the experimental resolution as defined above.

If a mass scan is obtained with a constant AC/DC ratio, the mass resolution \(\frac{m}{\Delta m}\) will remain constant. However, it is obvious that since \(m\) varies \(\Delta m\) must also vary to keep the resolution constant. This means that a different number of masses are stable in one point of the spectrum than in another. A much more desirable method of scanning would be one in which \(\Delta m\) is kept constant. In other words, the AC/DC ratio is gradually decreased with an increase in mass, in order to keep the length of the scan line inside the stability region constant. The results of the former method of scanning (i.e. constant scan-line slope) are presented in figures 8, 9 and 10. In figures 8a and 8b what appears to be a well resolved mode for the 18 peak is obviously a poorer resolution for the 28 peak and even worse for 44. In figure 8a the resolution is about 16 so that each individual mass number in that region is distinguishable; however, at \(m/e = 28\), \(\Delta m\) is about 2, so that mass numbers 27 and 29 are not well resolved. At \(m/e = 44\), "\(\Delta m\)" is approximately 3 indicating an even poorer resolution. Figure 8b shows a scan at a resolution of 20 to 25. In this case \(\Delta m = 0.7\) at \(m/e = 15\). Therefore only a fraction of the ions with \(m/e = 15\) would be seen. This lack of sensitivity is evidenced by the fact that mass numbers 12, 14, 15 and 17 were not detected, although they were at the lower resolution of 8a.

* See Figure 13
5.3 Ion Storage Characteristics

As has already been discussed, the pulsing procedure provides a direct control of the storage time of the trapped ions. Thus, for instance, an increase in frequency of drawout pulses decreases the storage time and vice versa. The basic procedure is then, to record peak height with variation in storage time (i.e. $1/f$). Such plots were obtained for the $N_2$ $m/e = 28$ peak at various pressures, as well as plots of various masses with approximately constant background pressure, and these may be found in Figure 14.

As expected, the peak height increases linearly with storage time reaching an upper limit. When saturation is approached the curve levels off and even begins to decrease slightly with further increase in storage time. The capabilities of the equipment prevented any further increase in storage time, although it is suspected that the peak height fluctuates about a level just below saturation. The slope of the linear portion of the curve may be varied by one or all of the following:

i) Filament current

ii) Filament potential

iii) Background pressure.

Such a finding is reasonable because a higher rate of ionization should result in a more rapid approach toward saturation of the ion trap. Figures 14 a and 14 b are examples of the variation of the slope with filament current and background pressure. Figure 14c indicates that the same general phenomena apply to various masses (i.e., $m/e = 14$, 16 and 44). Because of the uncertainty in the ionization current (as has already been discussed) it was not possible to absolutely calibrate the mass spectrum for various peak heights. And so, it must be pointed out that in figure 14c only the shapes of the curves are of any significance, while their relative magnitudes cannot be interpreted.

At the saturation level for $m/e = 28$, the multiplier output current was of the order of one microampere, for a pressure of $3.4 \times 10^{-7}$ torr. As the multiplier gain was approximately $10^4$, the multiplier input current was of the order of 0.1 nanampères. Therefore, the total saturation charge was of the order of $5 \times 10^{-15}$ coulombs, and the total number of ions trapped was approximately "$3 \times 10^3\". Using Dawson and Whetten’s criteria that only one tenth of the linear dimensions of the chamber is useful for ion trapping, the useful volume of the chamber was of the order of $8.5 \times 10^{-3}$ cc. Therefore, the saturation density of $N_2$ ions is found to be somewhat less than $4 \times 10^6$ ions/cc. This value compares favourably to a theoretical value obtained by Fischer(12), who considered the space charge effect as the primary factor for saturation. More recently Dawson and Whetten obtained a slightly lower concentration of $10^5$ ions/cc for $m/e = .28$ although they indicated that ion densities may reach as high as $10^8$ ions/cc.

VI. DISCUSSION

After the initial problems of obtaining a mass spectrum were solved, it was a simple matter to obtain a good mass scan between $m/e = 12$ and $m/e = 44$. * Filament current (fc) refers to the DC current passed through the filament, and is used as an indication of the filament emission.
However, because of the inability of the supply to operate in a constant \(\Delta m\) mode for the stability diagram of the three dimensional quadrupole, it was not possible to obtain a well resolved spectrum across the entire scan. In other words, if good resolution is required, the user would have to scan across a correspondingly smaller portion of the spectrum. This weakness appears to be a characteristic only of the specific quadrupole power supply used, and a supply built specifically for the 3-D quadrupole should overcome any such problems. (i.e., Such a supply should allow for a slight variation of the AC/DC ratio to keep \(\Delta m\) constant during mass scanning).

With regard to resolution, \(m/\Delta m\) ratios of greater than 200 were easily attained. In recording \(m/e = 28\) and \(m/e = 32\) by leaking in \(O_2\), a maximum resolution of 220 was obtained.

Storage characteristics were obtained which were very similar to those of Dawson and Whetten at General Electric. Such curves may be separated into three sections:

i) Linear increase of peak height with storage time

ii) Saturation (i.e., curve levels off with further increase in storage time)

iii) Slight peak height decrease.

Little is known about (iii) although it would appear that the curve fluctuates about some value below saturation. This is hinted at by the \(m/e = 16\) curve of figure 14c where, after an initial rapid decrease, the curve seems to flatten out.

At saturation, the maximum ion density was found to be of the order of \(10^6\) ions/cc. This value varied significantly through various reports. For example, although Dawson and Whetten observed a density of \(10^5\) ions/cc for \(m/e = 28\), they estimated that this value could be as high as \(10^6\) ions/cc. Dehmelt and Major(13) also measured \(10^5\) ions/cc, while Fischer predicted a density of \(4 \times 10^6\) ions/cc for krypton. All researchers to date have assumed space charge as the primary limitation on storage time.

Although studied indirectly, the sensitivity question seems to be reasonably clear. An indication of sensitivity was the fact that satisfactory spectra could be obtained using extremely low filament emission currents. With a DC filament current of 3.0 amperes, the operating point was at the very bottom of the emission curve of the tungsten filament.

The detection procedure in this study leaves much to be desired. The ions are pulsed out of the trap during a finite interval of time. What is seen at the multiplier output is a current whose magnitude is directly dependent on the time interval in which the ions are pulsed. If the interval is decreased, a higher current will be observed (assuming that all the ions are still detected), even though the total number of ions in the trap remains the same. Therefore, small fluctuations in pulse-width will show up as amplified current fluctuations at the multiplier output.

Rettinghaus (7) offered an interesting alternative to the pulsed detection method, using a resonant detection technique. With this method, an additional resonant circuit is placed between the two end-caps and is frequency swept. When the frequency approaches the resonant frequency of the trapped
species, the latter absorbs energy from the resonant circuit, and the energy loss may then be detected and related to the number of ions in the trap. With this method, Rettinghaus claimed that he detected as few as four ions in the trap.

Another area which demands more improvement is related to the ionization process. It has already been pointed out that diverging electron paths inside the trap make it extremely difficult to determine ionization cross-sections and therefore calibrate the mass analyzer.

It has been found by Harden and Wagner that the RF phase at which the ions are formed is very critical to the degree of stability of the ions. Figure 15 obtained from correspondence with Dr. Harden, demonstrates this relationship. They observed that the trapping efficiency was maximum when the ions were formed in phase with the RF. Although the experimental set-up did not provide for determination of the RF phase at ion formation, it is believed that the characteristic observed (i.e., peak shape change) with a variation of filament potential is related to this phenomenon. As the filament potential is increased negatively, more electrons enter the trap at, and near, zero RF phase, so that the trapping efficiency would be increased.

During the experiments already discussed, certain anomalies take on added significance due to correspondence with Dr. Harden. Dr. Harden reported that the system sometimes required as much as a half an hour to an hour prior to obtaining a stable peak shape. Experiments in this lab indicated that, although the times involved were not as great, a similar effect was observed. For example, if the m/e = 28 peak was to be studied, the power supply RF voltage would have to be left in the region of the m/e = 28 peak for a period of between 5 to 10 minutes before a satisfactorily stable peak could be obtained. After a stable peak shape was attained, it was possible to leave the m/e = 28 region and return to it within a reasonable time (e.g. several minutes) without losing its stability.

Another phenomenon was that the peak height obtained for a low to high mass scan was always smaller than that obtained in the reverse direction. However, the shape of the former was much more consistent. It is believed that this phenomenon may be due to a time-lag effect in the interval from the moment the ionizing beam leaves the filament to the moment the ions are trapped. Because the RF trapping field provides the accelerating potential for the ionizing beam, if the time-lag is significant, a down-scan (i.e. moving from a high mass to a lower mass) results in a higher density ionizing beam at a certain point of the mass spectrum than an up-scan at that same point. This would also explain the observation that the down-scans were more unstable than the up-scans. That is to say that the rate of approach of a certain point of the spectrum is more critical in a down-scan than an up-scan.

VII. CONCLUSIONS

The three dimensional quadrupole shows considerable promise of becoming a very high sensitivity universal trace gas analyzer. This was evidenced by the extremely low filament emission currents necessary to produce a mass spectrum. Because of its ability to trap a specific species for long periods of time the instrument may be used in extremely high resolution modes, especially when one is studying a single species.
The instrument's small dimensions will be of considerable advantage over the much bulkier quadrupole mass filter. Indeed, Dawson and Whetten have reported a 3-dimensional quadrupole of "3 cm x 5 cm" in size\(^1\); hand-shaped out of 20 x 20 stainless steel mesh. Also, unlike the magnetic sector mass spectrometers it does not contain magnetic fields which may disturb the multiplier.

However, there seems to be a considerable number of problems still existing in the day to day operation of a 3-D Quadrupole as a sensitive detector in a very highly sensitive trace gas analyzer as mentioned in the introduction. Also, a better understanding of the trapping mechanism should help in obtaining more stable mass spectra. It would appear that at least this latter problem is being studied extensively.
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ELECTRODE CONFIGURATION FOR A 3-DIMENSIONAL QUADRUPOLE

Figure 1

PULSING PROCEDURE FOR ION DETECTION

Figure 2

CONTROL PULSE

WITHDRAWAL PULSE

R-F
EXPERIMENTAL SET-UP FOR 3-D. Q. ION TRAP

Figure 3
SIGNAL PROCESSING CIRCUITRY

Figure 4

1. PREAMPLIFIER
   - $R_1 = 1.5 \text{ M}\Omega$
   - $R_2 = 20 \text{ K}\Omega$
   - $R_3 = 380 \text{ \Omega}$
   - $C_1 = 90 \text{ PF}$

2. COUPLING & DROPPING CAPACITORS
   - $C_2 = 0.1 \mu\text{F}$
   - $C_3 = 2.0 \mu\text{F}$

3. KAY 1024A AMPLIFIER

4. PEAK RECTIFIER
   - $D_1 = 1N4148$
   - $C_4 = 2.0 \mu\text{F}$
   - $R_4 = 1.5 \text{ M}\Omega$
STABILITY DIAGRAM FOR THREE DIMENSIONAL ELECTRODYNAMIC SUSPENSION

Figure 5

Figure 6  SCHEMATIC OF 3-D TRAP
Figure 7
Multiplier Output

(a) Amplifier Impedance 1 M ohms
(b) Amplifier Impedance 700 ohms
Pressure = 1.0 \times 10^{-7} \text{ torr}

Fill. Current = 3.0 \text{ amps}

(a)\[ \frac{1}{2} \]

(b)\[ \frac{1}{2} \]

MASS SCAN

Figure 8
PEAK SHIFT PHENOMENON (m=28)

FIGURE 9

DETAILED MASS SCAN OF m=14 to m=18

FIGURE 10
Figure 11
PEAK-SHAPE VARIATION WITH RESOLUTION

(m/e = 28, "R" is in arbitrary units.)

(a)  
R = 8.0

(b)  
R = 8.2

(c)  
R = 8.7
Figure 12
VARIATION OF PEAK-SHAPE WITH FILAMENT POTENTIAL (m/e = 28)

(a)
R = 8.6
f.c. = 2.85 amps
p = 5 x 10^{-8} \text{torr}
f.p. = -40 \text{volts}
f = 255 \text{Hz}

(b)
R = 8.6
f.c. = 2.85 amps
p = 5 x 10^{-8} \text{torr}
f.p. = -72 \text{volts}
f = 255 \text{Hz}
(Note: An increase in -ve f.p. allows an increase in resolution "R". Where "R" is in arbitrary units.)

(c)
R = 8.9
f.c. = 2.9 amps
p = 7.5 x 10^{-8} \text{torr}
f.p. = -100 \text{volts}
VARIATION OF STABILITY DIAGRAM
WITH MASS SCAN

Figure 13
STORAGE CHARACTERISTICS

(a) Effect of Pressure Increase

$m/e = 28$

Filament Current = 2.8 Amps

(b) Effect of Filament Emission Increase

$m/e = 28$

(c) Variation of Mass to Charge Ratio

Figure 14
Figure 15

PHASE DEPENDENCE OF PEAK HEIGHT ON IONIZATION PULSE

(Figure was obtained from correspondence with Dr. Harden.)
A new type of mass analyzer has been studied with a view to increasing discrimination and sensitivity capabilities. The three dimensional quadrupole mass spectrometer may be used as a universal trace gas analyzer or in the ion gauge mode as an ultra-high vacuum gauge. The instrument is capable of storing a specific mass-to-charge ratio or a range of such ratios for a sufficient time accumulating the species until they become detectable. The instrument was built and tested for practicality of operation, reliability and sensitivity. Results indicated that there are several areas of uncertainty in the operation of the instrument. The most significant of these were the ionization and detection processes. Otherwise, the instrument demonstrated its most useful capability of trapping and accumulating a species. This is seen as a significant step in the process of attaining higher degrees of sensitivity in trace gas analyzers.