In a mass spectrometer, a beam of gaseous ions are produced from a sample; the resulting mixture of ions is sorted out according to their mass-charge ratios, and output signals are provided which are measures of the relative abundance of each ionic species. Even though the classification of the mass spectrometers is based on their principle of operation, in general they are ion optical devices and mass-charge ratios are separated by utilizing electric and/or magnetic fields. The mass-charge ratios enable one to determine 'What' is present and the ion intensities themselves indicate 'How much' of it is present.

In general, one is interested in relative weights of atoms and molecules, than in their absolute weights. Therefore the concept of atomic mass unit (amu) is brought in. It is defined so that the mass of $^{12}\text{C}$ atom is exactly 12 amu and denoted as $m$. Therefore 1 amu = 1/12 the mass of Carbon. Using Avagadro's number

$$N_A = 6.02252 \times 10^{26} \text{ Kg mole}^{-1}$$

1 amu $= 1/N_A = 1.66043 \times 10^{-27} \text{ kg}$. 

The conversion equation is given as

$$M = m/1.6604x10^{-27}$$
When the term 'mass' or 'm/e' or 'M/e' are used in mass spectrometry m(M) refers to the sum of the mass numbers of the atoms composing the particular ion and 'e' refers to the number of electrons gained or lost, during ionization. A doubly charged ion exhibits an apparent mass, one-half that of the corresponding singly charged ion.

Any mass spectrometer must be treated as a system consisting a number of elements designed to carry out the determination of 'm/e' ratios along with their intensities. Regardless of the special design any instrument must comprise atleast four basic functional elements.

1) the ion source : Which provides representative ion samples.

2) the analyzer : Which effects separation in space or time.

3) the detector : Which detects the resolved ions and measures their intensities.

4) the vacuum system : Where the environment is provided.

In the upper atmospheric ion composition studies, the first and the last elements are provided by the atmosphere itself (above 100 km). While making the neutral measurements, the ion source is to be incorporated along with the system.
Mass spectrometers are in general classified into two groups; static and dynamic types.

The static type of instruments maintain their instrumental parameters constant and utilize the momentum and energy dispersion properties of the magnetic and electric fields respectively. There are many field combinations possible in such type of analyzers.

1.2 The dynamic type of instruments are, "Those instruments in which the time dependence of one or more parameters of the systems e.g. electrical field strength, magnetic field strength, or ion movement is fundamental to the mass analysis" (Blauth, 1966). The basic principle of mass separation is thus the time dispersion in the ion motion. Table 1.1 lists different types of dynamic instruments and their classification (Roboz, 1966).

**TABLE 1.1**

<table>
<thead>
<tr>
<th>Energy balance</th>
<th>Time of flight</th>
<th>Path stability</th>
<th>Characteristic frequency generator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear direct motion</td>
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<tr>
<td>Bennett</td>
<td>Ion</td>
<td>Smythe-Matta-uch</td>
<td>Klystron</td>
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<tr>
<td>Redhead</td>
<td>velocitron</td>
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<td>Topatron</td>
<td>Bendix</td>
<td>Monopole</td>
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<td>Linear periodic motion</td>
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<td>Palletron</td>
<td>Tempitron</td>
<td>Farvitron</td>
<td>Barkhausenkurz</td>
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<td>Double Well</td>
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<td>Quadrupole</td>
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<td>Reflektron</td>
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<td></td>
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<td>Ion cage</td>
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<td>Circular Periodic motion</td>
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<tr>
<td>Omegatron</td>
<td>Trojanon</td>
<td>Falk-</td>
<td>Magnetron</td>
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<tr>
<td>Trochoid-TOF</td>
<td>Synchrometer</td>
<td>Schwering</td>
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<tr>
<td>Synchometer</td>
<td>Hippie-Thomas</td>
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</tbody>
</table>
Of the several types of static and dynamic instruments only a few instruments have been successfully used for upper atmospheric studies; rest being more suitable to ground based, laboratory studies. The instruments chosen for the upper atmospheric studies should in general satisfy the following criterion; light weight, rugged, high current efficiency, large collecting area, repeatability and simplicity. The dynamic instruments satisfy these criterion and have found extensive usage as rocket and satellite payloads. The following sections, contain discussions, on one of the dynamic mass spectrometers, namely the Bennett type radio frequency mass spectrometer which was built and used in the course of present investigation.

1.3 Bennett-radio frequency Ion Mass Spectrometer

As listed in table I, this class of mass spectrometer falls under the heading of Energy Balance Devices. Here, energy is supplied to the ions in an interaction with a radio frequency field. Maximum exchange is achieved in the resonance condition, and mass scanning is facilitated by varying one of the mass dependent parameters in the resonance condition.

Built by Bennett (1950), this tube employs the principle of velocity selection. Constructionally it has parallel plane grids made with wire nets having a large transparency. The grids arranged in groups of three,
have a radio frequency alternating potential applied to the center grids. Retarding potentials are used to turn back all ions except those with the selected mass.

1.4 Theory of operation

1.4.1 Single stage tube

The theory of operation could be developed for a single stage tube and then could be extended to multistage tubes. A set of three grids is known as a stage (Bennett 1950). The single stage tube is illustrated in figure 1.1 (page 22a). Electrons from the filament 'F' are accelerated towards the first grid of the stage 'b' by the accelerating voltage applied to 'a'. These electrons collide with the neutral molecules present between 'a' and 'b' and eventually cause ionization, producing positive ions. The positive ions are accelerated towards the 1st grid of the stage 'b' by the potential 'V' applied to 'b' with respect to 'a'. The grids b, c and d are equally spaced at a distance 's'.

A radio frequency field with an angular frequency ' \omega ' is applied to the middle of the grids 'c'. The electric field between 'b' and 'c' would now be written as

\[ E_{bc} = E \sin (\omega t + \theta) \]  \hspace{1cm} \text{(1.1)}

and between 'c' and 'd' as

\[ E_{cd} = -E \sin (\omega t + \theta) \]  \hspace{1cm} \text{(1.2)}
't' is defined to be zero at the time the ion crosses the plane of the grid 'b'. $E \sin \theta$ will be the field at that instant, $\theta$ representing the phase angle.

It is assumed that the flow of the ions is uniform and ions enter the analyzer stage with all possible values of $\theta$.

As the ions pass the grids, because of the presence of 'rf', some will gain energy from and some will lose energy to the rf. A stopping potential, adjusted to be close to the maximum energy gain from the rf, is applied to the collector plate 'e'. The result being, only those ions which have gained near-maximum energy are allowed to get collected.

The assumption that, the change in velocity of an ion as it moves through the grids is small compared to its initial energy, reduces the complications in solving the motion of the charged particle in a sinusoidal field. The validity of the assumption has also been verified by experiments. Space charge effects are also neglected with negligible error for this system (Bennett 1950).

The force acting on a mass $m$ between grids 'b' and 'c' is

$$F_{bc} = m \ddot{x} = Ee \sin (\omega t + \theta) \quad \text{...(1.3)}$$

and between 'c' and 'd' being,

$$F_{cd} = m \ddot{x} = -Ee \sin (\omega t + \theta) \quad \text{...(1.4)}$$
Since the variations in the velocity of the ions due to the 'rf' is small compared to its average velocity between 'b' and 'd', the energy gained by the ion from the oscillating field could approximately be written as

$$\Delta W = \Delta \left( \frac{hv^2}{2} \right) = \nu \cdot \Delta (hv) = \nu \cdot \int F \cdot dt \quad (1.5)$$

The transit time for the ion to travel from one grid to the other is \( s/v \) where 's' is the distance and 'v' is the velocity.

Substituting the values for \( F \) in (1.5) with the proper limits

$$\Delta W = \nu \left\{ \int_0^{\frac{2\pi}{\nu}} Ee \sin(\omega t + \theta) \, dt + \int_{\frac{2\pi}{\nu}}^{\frac{\pi}{\nu}} -Ee \sin(\omega t + \theta) \, dt \right\} \quad (1.6)$$

Integrating and substituting the limits,

$$\Delta W = \frac{Eev}{\omega} \left[ \cos \theta - 2 \cos \left( \frac{\omega}{\nu} + \theta \right) + \cos \left( \frac{2\pi \omega}{\nu} + \theta \right) \right] \quad (1.7)$$

\( \Delta W \) will be maximum with respect to variations in when

$$\frac{\omega}{\nu} + \theta = \pi \quad (1.8)$$

which means that the ions which pass through grid 'c' just as the field reverses, obtain the maximum incremental energy. The expression for \( \Delta W \) is maximum with respect to variations in \( \omega \) when
This quantity $\Delta \omega / \nu$ is known as the 'transit angle' or 'tuning' parameter.

The velocity of the ion which gains maximum energy is obtained from

$$eV = \frac{1}{2} M m_0 \nu^2 \quad .....(1.10)$$

where 'V' is the potential difference between the ion-source 'a' and the grid 'b'. $M$ is the atomic mass number of the ion; 'm_o' is the mass of an ion of unit mass number.

Eliminating '$\nu$' from the last two equations $(1.9)$ and $(1.10)$

$$M = \frac{0.266 \times 10^{12}}{s^2 f^2} v \quad .....(1.11)$$

where $V$ is in volts, 's' in centimeters and 'f' in Hz.

Figure 1.2 (page 22a) is a plot of the incremental energy $\Delta W$, gained by an ion passing the grid 'c' at $180^\circ$ phase as a function of the number of cycles 'N' executed by the alternating field while the ion travels from grid 'b' to 'd'. The principal maximum of this curve is at $N = 0.74$ cycle, because the transit angle from the first to the third grid for maximum $\Delta W$ is
Fig. 1.1: Schematic representation of a single stage Bennett spectrometer.

Energy Gain - Single Stage

Fig. 1.2: $\Delta W$ - the energy acquired by an ion passing the grid C, at 180° phase as a function of the number of cycles $N$ (Bennett 1950).
\( \frac{2 \Delta \omega}{\nu} = 267^\circ = 0.74 \text{ cycle} \quad \ldots (1.12) \)

in terms of the tuning parameter \( \Delta \omega / \nu \)

\( \frac{\Delta \omega}{\nu} = 2.34 \text{ radians} \quad \ldots (1.13) \)

If the retarder voltage is set to reject those ions which have received energy less than \( k \Delta W_{\text{max}} \) where \( k \) is a fraction, the ions specified by values \( 'N_1' \), to \( 'N_2' \) will continue their path to the detector. As the retarder constant \( 'k' \) approaches unity, \( N_2 - N_1 \) decreases and consequently the mass resolution of the analyzer increases. The subsidiary maximum in figure 2 refers to the energy gained by harmonically synchronous ions corresponding to a different tuning parameter, i.e. by the time the ion takes to reach from \( 'b' \), to \( 'd' \) the \( 'rf' \) would have executed nearly 3 cycles. The height of this maximum places a lower limit on \( 'k' \) if harmonic peaks are to be excluded from the mass spectrum.

It has been found by experiment that the above approximate treatment is adequate, if the d-c potential difference between the source and the first grid is more than 10 times the amplitude of the rf alternating potential. If the rf amplitude is more than this value then it results in irregular mass peaks. However, symmetric peaks up to about half the d-c potential could be obtained if the d-c potential on grid \( 'c' \) (to which the a-c potential is added) and on grid \( 'd' \) are reduced by just the amount necessary to reduce
the speed of an ion receiving maximum incremental energy,
back to the same speed as that with which the ion entered
the analyzer stage. The reduced potential is referred to
as 'bias'.

The choice of the retarding potential values is
made on the basis of the maximum energy gained by the
ions. If the grids were ideal (very small holes, compared
with the inter grid distance), the maximum incremental
energy an ion could acquire from the rf field would be
about the same as acquired from a d-c potential twice
the rms., value of the rf potential on the centre grid.

1.4.2 Two Stage Tube

The above treatment could be extended to multistage
tubes also.

The configuration of the grids are schematically
represented in figure 1.3 (page 25a ) for a two stage
tube. 'FF' is the filament, 'a' the electron accelerating
grid b,c,d the first stage and 'e' 'f' 'g' being the second
stage. To the grid 'h' is given a stopping potential and
'p' is the collector. 'c' and 'f', the centre grids of
the two stages carry the radio frequency field superimposed
on the dc accelerating potential. The grids 'd' and 'e'
are at the same potential providing a field free drift
space. The drift space distance 'de' is adjusted such that,
an ion receiving maximum incremental energy from the first
stage will reach the initial grid of the second stage 'e'
at the right phase of the 'rf' alternating potential to acquire maximum incremental energy from the second stage also. The rf must execute exactly integral number of rf cycles by the time the ion traverses the distance 'c' to 'f', in order to accomplish the above said criterion. Therefore, the distance between 'd' to 'e' in terms of 's' the distance between the grids in the analyzer stage could be written using equation 1.9.

\[
\frac{2\pi}{\nu} = 134^\circ; \quad \frac{2\pi}{\nu} = 0.7444 \text{ cycle}
\]

1 cycle \(= \frac{2}{0.7444} \times s = 2.67 \text{ s}\)

n cycle \(\approx 2.70 \text{ ns}\)

This corresponds to the distance between the center grids of the two stages.

Therefore the distance between 'd' to 'e' must be

\[(2.70 n - 2)s\]  \hspace{1cm} \ldots \ldots \text{(1.14)}

Where 'n' is an integer, 's' the distance between the grids in each stage as before. The multistage tube, for example a two stage tube, is known as 'n' cycle - two stage tube.

The incremental energy which can be acquired by an ion from both the stages of a two stage tube is illustrated in figure 1.4 (page 25a). The envelope of the curve is the same kind as in figure 2 but with twice the ordinate. The addition of one more stage results in
Fig. 1.3: Two stage schematic of a Bennett tube: The two stages are separated by a field free drift space.

Fig. 1.4: The incremental energy acquired by an ion from both the stages as a function of rf cycle.
sharper peaks. But the disadvantage of the two stage tube being that large peaks occur for frequencies corresponding to other numbers of cycle between stages close to the number corresponding to the principal peak and much of the sensitivity is lost in increasing the retarding potential in order to cut off the adjacent peaks.

1.4.3 Three Stage Tube

This is one of the most popular version of the Bennett type Mass Spectrometer. This combination is observed to retain much more sensitivity and at the same time produces only a single peak for each mass. The distance between the stages are governed by the earlier criteria that the 'rf' executes exactly integral number of cycles while the ion which has gained maximum energy travels from one stage to another. The integral numbers between stages are so selected as to avoid any appreciable overlap of the harmonic peaks of the pair of stages considered as two-stage combination. When the integral numbers are so chosen, much more of the peak can be made to appear above the blocking potential, than with either a single or two stage combinations. This eventually increases the sensitivity of the system.

The device which was built by the author and used in the present investigation was a three-stage tube, the details of which are discussed in later sections. The typical $\Delta W \nu_g N$ curve is depicted in figure 1.5 (page 28a)
which clearly shows the superiority of the device over the single and two stage tubes.

1.5 Performance of the Bennett-type radio frequency mass spectrometer

The performance of any instrument is based on the resolution and sensitivity. All such instruments eventually measure the ion current. The term 'current efficiency' is also often used. The performance of a five-stage tube has been discussed by Wherry and Karasek (1955). Vorsin and Doil'ntsyn (1959) have presented a comprehensive treatment of the axial field rf mass spectrometer which permits a detailed evaluation of any proposed electrode configuration. They have derived expressions for the theoretical mass resolution \( M/\Delta M \) and current efficiency \( \eta \),

\[
\frac{M}{\Delta M} = \frac{\gamma_0}{4 \sqrt{2}} \left[ \frac{q^2}{12 (1-k)} + \left( \frac{2\pi}{\gamma_0} \right) \right] X
\]

\[
\frac{n_1^2 + n_2^2 + \ldots + n_p^2 + (n_1+n_2)^2 + \ldots + (n_{p-1}+n_p)^2 + \ldots + (n_1+\ldots+n_p)^2}{(p+1)^2 (1-k)}
\]

\[
\ldots \ldots (1.15)
\]

and

\[
\eta = \sqrt{\frac{2(1-k)}{\pi}}
\]

\[
\ldots \ldots (1.16)
\]
where \( q+1 \) = the number of grids in a stage

the gaps being 'q'

\[ \gamma_o = \text{the tuning parameter} \]

\[ \gamma_o = 2.34 \text{ if } q = 2 ; \quad \gamma_o = 2.93 \text{ if } q = 4 \]

\( p+1 \) = the number of stages

\( p \) = the number of drift spaces

\( n_1 \ldots \ldots n_p \) = the number of rf cycles corresponding to the stage separation.

From the mass resolution equation 1.15 , it is seen that any increase in \( n_p \) the cycle numbers tends to improve resolution. The heights of harmonic maxima are the ones which restrict the choice of \( n_p \). If \( k = 0.9 \) (90% of the \( \Delta W_{\text{max}} \)) then a typical resolution of '20' is obtained for a three stage tube.

The use of non sinusoidal voltage such as \( V_o (\sin \omega t - \sin 2 \omega t) \) instead of \( V_o \sin \omega t \), is observed to increase the resolution by a factor of 2.8, as shown by Dekleva and Peterlin (1955). One of the studies by the author has revealed (Sridharan 1981) that replacement of the suppressor potential by means of a sweep increases the resolution by about 25% in the high mass side.
Fig. 1.5: The incremental energy acquired by an ion from a three-stage cyclotron.

Fig. 1.6: Calculated values of mass number vs. resolution. (Kenesky and Karasuk 1955)
Wherry and Karasek (1955) have studied the resolution properties of a 5 stage tube which is applicable to a three stage tube as well. The resolution increases with the increase of \( k \) in the retarding potential. The resolution \( V_g \) mass number is shown in figure 1.6 (page 28a). It is to be noted that \( M/\Delta M \) is a function of mass number, becoming more for higher masses. With a larger retarding potential it turns out to be fairly uniform for high mass side.

In figure 1.7 (page 29a) is shown that the incremental energy gained by adjacent ions, indirectly indicated the value that must be chosen for the stopping potential. Mass number 40 is shown to acquire \( >90\% \) of the energy gained by 41 amu though the instrument is tuned to 41 amu. In order to resolve 40 and 41 amu one has to choose stopping potential larger than the potential corresponding to the energy gained by 40 amu (Wherry and Karasek, 1955).

1.6 **Current efficiency**

For perfectly transparent grids, the current efficiency of the analyzer calculated using equation 1.16 would be 0.14. In practice each of the modulator grids transmits 95\% of the ions. Therefore, the current efficiency becomes \( 0.95^a \times 0.14 \). Where \( \text{a} \) is the total number of grids the ion has to pass through. In figure 1.8 (page 29a) is shown the relation derived by Wherry.
Fig. 1.7: Energy gained by the adjacent ions through the analyser tuned to 41 amu.

Fig. 1.8: Variation of the sensitivity with mass number (amu) for various stopping potential.
and Karasek (1955), between the mass number and the current efficiency for different retarding potential values. Further the efficiency of the instrument is known not to be the same for all masses. The relative efficiency $V_s$ mass number is depicted in figure 1.9 (page 30). For lighter masses the efficiency is poor and is fairly uniform for higher masses. This aspect is important when absolute or relative density measurements are to be made in a mixture of light and heavier species.

**1.7 Effect of finite 'rf' amplitude**

In the earlier discussion it had been assumed that the 'rf' amplitude is small compared to the dc accelerating potential. In the actual case this is not so. This modification has been incorporated in the final expression for $M$, (Johnson, 1960).

$$M = \frac{0.266(V + 2.05 V_{\text{rms}})}{s^2 f^2}$$  \hspace{1cm} (1.17)

The term $2.05 V_{\text{rms}}$ is the potential through which the selected mass falls through, due to rf.'s' is in cm$s$ and 'f' is in MHz.

**1.8 Effect of rocket potential**

If the rocket vehicle containing the spectrometer acquires a charge while in the ionosphere, the term 'V' in equation 1.11 should be modified to take into account
of this factor too. A negative charge on the rocket would result in a mass scale shifted toward the lower mass side relatively. The effective stopping potential would also be reduced. This vehicle potential creates a problem in choosing the proper setting of the retarding potential. The modified equation takes the form

\[
M = \frac{0.266(V + kV_{rp} + 2.05 V_{rms})}{s^2 f^2}
\]

where \(V_{rp}\) is the rocket potential due to a negative charge and \(k\) is the fraction which takes into account the point in the field where the ion was created or where it experienced its last collision.

1.9 Absolute mass determination of the ions

In rocket ion mass spectrometry the ion source used for laboratory calibration is detached from the tube and the ionosphere provides the ions. Since the mass scale of a Bennett tube is dependent on the ion entrance energy this change of ion source requires a method whereby the absolute mass of ions, detected during flight could be determined. Johnson (1960) has devised a method by making use of the harmonic ions. These are ions which travel the different stages in near integral number of rf cycles and gain nearly 85% of maximum energy. By defining a parameter \((1 + h_a)\) as harmonic ratio, the fundamental and the harmonic peak are shown to occur at related voltages. By substracting
any one of these voltages from another the absolute mass of the unknown ion can be determined in terms of known parameters, irrespective of the unknown energy of the ions.

Thus the mass of the unknown ion in terms of the voltage difference between its fundamental and a lower harmonic peak is given by

\[ M = \left( \frac{0.266 \times 10^{12}}{s^2 f^2} \right) \left( \frac{(v_s - v_{sha})}{1 - \frac{1}{(1 + h_a)^2}} \right) \text{ amu} \quad \ldots \ldots (1.19) \]

where \( v_{sha} \) is the potential corresponding to the harmonic ions (Johnson 1960).

The first quantity on the right hand side is known as the proportionality constant of the spectrometer. The proportionality constant and the harmonic ratio must be determined for each instrument under actual operating conditions. This technique is observed to resolve several ambiguities in mass determination.

1.10 System details (Ion mass spectrometer)

The mass spectrometric system used in the present study of upper atmospheric composition is represented schematically in figure 1.10 (page 32a). The electronic circuits are represented in blocks and are discussed in detail in later sections.
Fig. 1.9: Mass discrimination of the analyzer i.e. relative efficiency of the mass tube for light and heavy masses.

SCHEMATIC - THREE STAGE BENNETT TUBE

Fig. 1.10: Schematic representation of a 3-stage Bennett mass spectrometer along with the associated electronics blocks.
Essentially this analyzer tube is a 7+5 cycle type. The first two are the ion accelerating grids \((G_1 \text{ and } G_2)\) and are given potentials of the order \(-8V(G_1)\) and \(-80V(G_2)\). This ensures fairly uniform energy distribution of the ambient ions. '\(G_3\)' is the first grid in the analyzer stage to which a dc accelerating voltage, in the form a sweep is applied. The repetition rate of the sweep being 1.2 to 1.5 sec. (-80 to -500 volts). To the center grid is applied a radio frequency of 5 MHz with a peak to peak amplitude of 10 volts superposed over the dc sweep. The electrical connections between the grids are also depicted in the diagram. The distance in terms of rf cycle between the central grid of the first stage to that of the second stage is 7 cycles. In order to make the drift space equipotential the first grid \((G_5)\) of the second stage is connected to \(G_5\) of the first stage. The third stage is separated by 5 cycle distance from the second stage. Succeeding the third stage, a set of stopping potential grids are provided. Three such grids kept at the same potential enable a very sharp cut off. This is followed by a suppressor grid \((-550V)\) and a Faraday cage collector. The collector plate is kept in a cage completely shielded and floating. The plate is well insulated from the surrounding cage; insulation resistance being \(>10^{12} \Omega\). The whole structure is kept in a stainless steel enclosure and all the electrode leads and brought out by suitable vacuum feed throughs. The grid rings are made up of
stainless steel to which very well stretched gold plated tungsten mesh (50x50), is spot welded. The optical transparency of the grid is well over 90%. The grid thus prepared provides a good approximation for an equipotential surface. The grids are separated by PTFE spacers. The complete inner assembly is shown in figure 1.11 (page 34 a). The complete system with electronics package is depicted in figure 1.12 (p. 35a). The choice of the materials were carefully made so as to comply with the following requirements.

1.11 Choice of materials for construction

The materials used,
1. must be sufficiently gas tight, with no porosity,
2. must have very low vapour pressure,
3. must not evolve excessive adsorbed gases,
4. must withstand a degassing process at elevated temperatures.

Apart from these the magnetic properties of the materials must also have to be taken into account. High alumina content ceramic, teflon, stainless steel, and gold plated tungsten were the materials used in the construction of the sensor.

1.12 Control circuits

The basic electronic circuits needed for a complete system are listed below:
Fig. 1.11: A photograph of the inner structural assembly of the three stage Bennett mass spectrometer built by the author.
1. Ion accelerating and suppressor voltage generator with outputs of (i) -8V, (ii) -80V, (iii) -550V.

2. High voltage linear sweep generator with a d-c sweep from -80V to -500V with a duration of 1.2 to 1.5 sec.

3. Stable *rf* frequency generator with a frequency of 5 MHz and a peak-peak amplitude of 8-10V.

4. Current to voltage converter capable of measuring 1 pico Amp (10^-12 Amp) with a dynamic range of 3 orders of current (upto 1 nano Amp (10^-9 Amp))

5. Automatic gain switching amplifier with a dynamic range of 5 orders (from 1 mv - 10 V).

In space borne probes, the circuits have to fulfill special requirements. Apart from having light weight and small volume, the power consumption must also remain low. All the circuits must be capable of operating at low voltages which can be derived from d.c batteries. The circuits used in our present study were operated on + 12 volts which were derived from rocket batteries. The details of the different circuits are discussed below.

1.12.1 Ion acceleration and Suppressor Voltage Generator

The required voltage (-8V), (-80V) and (-550V) are generated by a dc-dc converter using AM20 Arnold toroidal core for the transformer. There are two secondary windings one for high and one for low voltages. The number
Fig. 1.12: Photograph showing the complete system along with the electronics package. The current to voltage converter and the rf oscillator are housed right behind the analyzer.
of windings in the collector are adjusted such that the frequency of operation is kept low (<5KHz) so that interference with the telemetry VCO channels could be avoided. The circuit diagram is given in figure 1.13 (page 36a). On the secondary side voltage doublers are used to obtain the required voltages. Since the current drawn is fairly small i.e., < 50 mA, no special arrangements to regulate the voltages is called for. The circuit is found to be efficient (>80%) and fairly stable.

1.12.2 High voltage sweep generator

Since the mass number reaching the collector is linearly proportional to the accelerating voltage a linear sweep would greatly simplify the mass analysis. The circuit built for this purpose operates on the miller integrator principle. A dc-dc converter is also brought into the feedback loop of the integrator. The dc-dc converter is similar to the earlier design. A part of the sweep is continuously monitored and as soon as it exceeded the preset value, a hermetically sealed relay across the charging capacitor, is operated and the capacitor discharged. The circuit is regenerative and the whole operation repeats itself. In this circuit there is flexibility to adjust the tripping voltage by varying the comparator reference and the period of operation is effectively controlled by varying the feedback resistance. Figure 1.14 (page 36a) is the actual circuit diagram used in the present system. The lower
SUPPRESSOR AND ACC. GRID VOLTAGES

Fig.1.13: Circuit diagram of the d-c supply; ion acceleration (-8V and -80V) and suppressor potential (-550 V) are derived from the same.

Fig.1.14: A linear regenerative sweep generator (-80V to -500V) of period (~1.5 sec). The bottom portion is a tristable circuit used in programming the retarding potential values.
part of the diagram is a tristable circuit which is used in programming the stopping potential values in order to obtain different sensitivities and resolution in consecutive sweeps.

1.12.3 RF Generator

This forms an important circuit in the system which essentially controls the resolution of the mass tube. The frequency must be maintained stable (<1%) under the changing environmental conditions encountered in rocket flights. A Hartly Oscillator is chosen for its known frequency stability (∼0.1% deviation). A buffer amplifier is used to isolate the main oscillator from the loading elements. The driver amplifier is driven by a constant current source. The bias for this source is derived from the rf voltage itself. Further, the retarding potential that governs the resolution of the sensor is also derived from the rf voltage. The advantage of this being that in case due to some reason the amplitude of rf voltage goes down, then it would reflect in the energy gained by the ions. As a result the sensitivity of the system would go down drastically. If the retarding potential is derived from the rf voltage itself, then there would be a corresponding decrease in the retarding potential which would take care of the loss in sensitivity. Further, in order to obtain symmetric peaks, the dc equivalents of rf voltage is substracted from the sweep (bias) and applied to the last grids of different stages. All these features are incorporated in the circuit depicted in figure 1.15 (page 38a).
1.12.4 Current to voltage converter

In actual operation, at the collector we get the ion current which is of the order of pico Amperes. The amplifier used to measure this low current should then have an extremely large input impedance. 'Intersil 8500 A' amplifier has been chosen for this purpose. The input impedance of this MOSFET input operational amplifier is $10^{14} \Omega$, with a typical bias current being 0.01 PA. In conjunction with this operational amplifier a feedback resistance of $10^{10} \Omega$ enabled one to measure currents as low as pico Amperes. Also to overcome the problem of dc drift of the circuit, which is one of the critical problems of low current measuring devices, a feedback network which automatically corrects the drift at the end of every sweep and stabilised the whole circuit with respect to environmental changes, is also incorporated. The circuit diagram of this part is shown in figure 1.16 (page 38a).

1.12.5 Automatic gain switching amplifier

From the requirement of rocket FM telemetry one has a limitation that the output signal amplitude fed to the telemetry should not be larger than 5 volts. Therefore, in order to increase the dynamic range one has to resort to different techniques. Use of logarithmic amplifier which has an output swing of 1 volt per decade current change is one of the methods of overcoming this difficulty.
Fig. 1.15: A highly stable rf oscillator (~5 MHz). The retarding potential is also derived from rf.

Fig. 1.16: A very high input impedance (~10^{14} \Omega) current to voltage converter with automatic off-set control.
However, the error involved in reading the data will be large as the amplitudes of the signal increases. In the present case there are four amplifiers with different gains from high to low, continuously operating parallelly and the output of these amplifiers are automatically switched to lower gain outputs as and when the higher gain outputs reached 5 volts. A flag output represented by a dc level indicates the gain settings. The details of this circuit are given in figure 1.17 (page 39a).

A typical mass spectrum obtained in one of the flights, by the mass spectrometer fabricated by the author, is depicted in figure 1.18 (page 39a). The main amplifier output, the flag output and the sweep monitor are clearly seen in the telemetry record.

1.13 Conversion of collector current into ion densities

Though in most of the cases the measured masses are treated only on the basis of their relative importance some times it becomes necessary to obtain the absolute concentration. In actual experiments the total ion currents would be normalised to the total ion densities measured by means of suitable probes. However, it is also possible to arrive at the absolute densities with a knowledge of the spectrometer parameters. This involves parameters which are effective inside the sensor as well as those which control the effective collection area associated with the sensor orifice (Taylor et al 1963).
Fig. 1.17: An automatic gain switching amplifier with 3 orders of dynamic range.

Fig. 1.18: A typical sample spectrum obtained from one of the flights.
The current collected $I_c$ is a fraction of the input current as the rest is lost to the sensor itself

$$I_c = (0.95)^a \times 0.14 \times I_o \quad \cdots \quad (1.20)$$

$(0.95)^a \times 0.14$ is the spectrometer efficiency factor and $I_o$ is the current input.

The expression applicable for a planar probe may be used as a first approximation:

$$I = \frac{n_i e a' A}{2 \sqrt{A}} \quad \cdots \quad (1.21)$$

where $n_i$ is the ion density (ions/cm$^3$), $a'$ is the most probable ion velocity and $A'$ is the area of the orifice grid.

In a rocket flight $I_o$ is influenced by the draw-in potential ($E_o$) and the angle of attack $V_r$. Incorporating these quantities

$$I_o = \frac{n_i e a' A}{2 \sqrt{A}} f(E_o, V_r) \quad \cdots \quad (1.22)$$

when the draw-in potential is sufficiently large, due to the relatively low velocity of the vehicle at the peak altitude $f(V_r)$ could be dropped. An approximation of $f(E_o)$ based on consideration of the orifice geometry and fringing field results in $A_{eff} = 3A$.

Therefore the final expression could now be written as
where \( A \times f(E_0) = A_{\text{eff}} \)

1.14 Operation

For any mass spectrometer to perform, the following points are important: The loss of ions within the spectrometer should be minimum. This means collisions of the particle with themselves should be low which essentially determines the operating pressure. The mean free path (\( L \)), which is defined as the distance between two successive collisions must be larger than the dimensions of the analyzer. This parameter is defined as

\[
L = \frac{1}{\sqrt{2} N \pi d^2} \text{ Const} \frac{1}{p} \quad \ldots (1.24)
\]

where

- \( n \) = number of molecules per unit volume
- \( d \) = molecular diameter
- \( p \) = pressure in the system

The term \( \sqrt{2} \) enters on account of Maxwell Boltzmann distribution of molecular velocities (Roboz 1963).

The mean free path is inversely proportional to pressure at constant temperature.

An useful practical form of the above equation is \( L = 5/p \) for Nitrogen (\( N_2 \)): \( p \) is measured in microns (\( 1/\mu = 10^{-4} \text{ cm} \)) and \( L \) in cms.
The mean free path for ions is given as

\[ L_{\text{ion}} = \sqrt{2} L \quad \text{and} \quad \ldots \quad (1.25) \]

\[ L_{\text{electron}} = 4 \sqrt{2} L = 5.66L \quad \ldots \quad (1.26) \]

where \( L \) refers to the mean free path of the neutrals.

In reality, because of the chaotic nature of the molecules, the free path of individual molecules varies from zero to infinity. The number of molecules \( n_m \) able to traverse a distance 'L' in a gas without collision is given by

\[ n_m = n e^{-1/L} \quad \ldots \quad (1.27) \]

These facts are important in the design of ion sources to be discussed in a later section.

Since the instrument used in the present study was about 20 cm long, the operating pressure could easily be obtained from the mean free path considerations as \( \sim 3 \times 10^{-3} \) mm(torr) or 3 microns. In terms of altitude it corresponds to above 90 km from sea level.

1.15 Vacuum system

In order to operate and calibrate the mass spectrometer a suitable vacuum system was used, which provided the necessary environment. A rotary pump and an oil diffusion pump combination with liquid \( \text{N}_2 \) trap, enabled to reach up to \( 10^{-6} \) torr in the high vacuum range. An ion source, of hot filament type provided the necessary
ion flow which were later analyzed by the instrument. Through fine leak valves different gases could be let in at different pressures for calibration purposes.

Even though the system used reaches vacuum levels of the order of $10^{-6}$ torr, there is always the possibility of backstreaming of oil vapours into the system which eventually contaminates the sensor part.

To avoid such contamination, the system to be used with a mass spectrometer must be 'clean'. Two sorption pumps operated in tandem mode had also been used with success. Sometimes a sputter ion pump backed by a rotary and diffusion pump combination is also used. The vacuum obtained in these systems are relatively free of hydrocarbons. The normally used laboratory set up is depicted in figure 1.19 (page 43a).

1.16 Neutral mass spectrometer

The basic ion mass spectrometer can be conveniently extended to measure neutral composition as well. For this purpose a suitable ion source must be incorporated in the spectrometer itself. Necessary biasing must be done at the entrance aperture of the instrument, at the time of neutral measurements. Ions produced at the source would then be driven into the analyzer section and would mass analyzed. One such instrument was built and flight tested. The ion source that was built in, was designed to satisfy the following basic requirements.
Fig. 1.19: The complete laboratory test set up of the Bennett mass spectrometer.
1. The supply of ions should be sufficiently intense to be compatible with the analyzer geometry and detector sensitivity.

2. The energy spread of the beam must be small.

3. High percentage of the sample must be analyzed.

4. The sources should not have a memory that would yield ions from the contamination of prior analysis.

5. Ion emission should reasonably be stable with time.

1.17 Some of the different types of ion sources available are listed below:

1. Vacuum spark sources

   **Advantages**
   - Sensitivity does not depend on elements by more than an order of magnitude.

   **Disadvantages**
   - Large energy spread of the ions (>1000 eV) which makes double focussing absolutely necessary.

2. Thermal Ionization Source

   - Relatively free background. Smaller quantity sample is sufficient. Energy spread is small.
   - Ionization efficiency is different for different elements and ion emission is not very stable.

3. Gas discharge type

   - Provides a large ion current and simple to construct.
   - Discharge is unsteady. A large sample is required. It cannot be used in high vacuum. Energy of the ionizing electrons cannot be controlled.
iv. Photoionization source

Photoionization cross section is smaller (< 2 orders) compared to electron cross section. Therefore selective ionization is possible.

v. Electron impact type

One of the most popular ion sources which was chosen for its relative merits.

Electrons emitted from a hot filament are accelerated by suitable fields and the resulting collisions between the neutral molecules yield a copious amount of ions. Suitable materials with a smaller work function, such as Tungsten, Thoriated tungsten, Rhenium etc., could be used as filament materials. These sources have the inherent advantage, that the energy spread of the ions is fairly low and the energy of the ionizing electrons could also be controlled. By including the ion emission current in the feedback loop of a circuit which controls the electron emission, very stable ion beams could be obtained. Figure 1.20 (page 45a) depicts the ionization efficiency curves. The neutral mass spectrometer schematic and the photograph of the actual system built are shown in figure 1.21 (page 46a) and
Fig. 1.20: Ionization efficiency curves for inorganic gases (Roboz 1968).
1.22 (Page 46 a) respectively. The system could conveniently be used to measure ion composition also. At the time of ion measurements the bias on the entrance grid is suitably modified and the ionizing electron beam is deflected in the opposite direction, thus enabling one to program ion/neutral measurements.

1.18 Structural details

The hot filament ion source built in the present case is a compact one and has the following features. The cross sectional details are depicted in figure 1.2f (page 46a). The filament (F) used is a tungsten wire of 75μ; dia and about 2.5 cm long. When about 1.2 Amp is passed an electron emission of 100 μA is realised at the accelerating grids. There is a channel made up of stainless steel behind the filament. A potential of -100 volts is applied to the channel. This negative potential drives all the electrons towards the ionizing region. The filament is followed by two grids kept at the same potential (+50V). These grids guide the electrons to the ionizing region. On top there is a grid which is given a positive potential and the ions once produced are pushed down to the analyzer. The anode is kept at a slightly larger positive potential compared to the ion repeller grid. The electrons complete the circuit at the anode. When the instrument is to be operated in the ion mode then the following changes are made in the potential configuration.
Fig. 1.21: Schematic representation of a neutral mass spectrometer with an inbuilt ion source.
Fig. 1.22: Photograph of the actual instrument built by the author.
1. Ion repeller potential is removed and replaced with an ion inlet potential.

2. The channel -100 V is replaced by a positive potential thus attracting the electron beam instead of repelling it.

3. The electron accelerating grid potentials are removed from the grids.

These changes are easily accomplished by means of a quenching pulse derived from the sweep circuit, thus enabling one to choose between the two modes in alternate sweeps.

Conclusion

The Bennett radiofrequency mass spectrometer system was discussed in some detail. Large amount of data had been obtained using this technique all over the world. Most of the composition informations obtained are used in their relative form. As had been pointed out, though it is in principle possible to obtain absolute densities, there are large uncertainties involved, in the trajectory and attitude of the vehicle. Therefore, it is customary to measure the total ion/electron densities along with, and the sum of the individual peaks normalised to these values in order to obtain individual absolute concentrations.
In the case of neutral measurements, the efficiency of the ion source under varying conditions must also be known in order to evaluate the absolute densities. Therefore, it is customary to study the neutral constituents only in their relative form to eliminate such uncertainties.