

PARTIAL PRESSURE MEASUREMENT

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Abstract

The quadrupole mass spectrometer is now well established as the instrument used almost universally for partial pressure measurement. This spectrometer can be considered as a hot-cathode extractor ionisation gauge with the addition of an electrostatic mass filter between the ion source and the ion collector. This filter consists of a square array of circular rods approximately 6 mm diameter and between 100 to 150-mm long. Positive ions are injected parallel to the central axis towards the ion collector. A filtering action is achieved by applying combined radio frequency and dc potentials between opposite pairs of rods. The characteristics of the filter can be controlled by small changes in the relative values of the radio frequency and dc voltages and the mass range by changes in the frequency of the ac signal. Care must always be taken when operating this mass spectrometer in an analytical mode because of non-linearities caused by space charge and other effects which are important, particularly in the injection region between the ion source and filter. Also the filter is subject to loss of sensitivity over the long term, generally caused by contamination from hydrocarbon impurities in the vacuum system. This is not normally a problem in ultra-high vacuum operation. Although almost all filters have been designed to operate with relatively low voltages applied to the rods, alternative modes are being considered which require distinctly high voltages or lower frequencies. There are hopes that these will have advantages for general operation.

1. INTRODUCTION

There are a number of different types of mass filter — mass spectrometer — that have been considered for the analysis of the gases found in vacuum systems. All are based upon the hot cathode ionisation gauge, with the addition of some form of mass filter placed between the ionisation chamber and the ion collector. The pressure range to be considered is from approximately 10^{-4} mb down to ultra-high-vacuum. The four instruments that have been responsible for the major share of the development are:

- The magnetic deflection mass spectrometer
- The Omegatron
- The time-of-flight mass spectrometer
- The quadrupole mass filter

All have the advantages and disadvantages of hot-cathode devices (e.g. problems due to filament outgassing) and all operate over roughly the same pressure range.

Not surprisingly the magnetic deflection mass spectrometer, because of the general interest in its performance, was the first instrument to be used. Developments were particularly significant during the period 1940 to 1960. Figure 1 illustrates the principles of operation of the 180° deflection instrument. The positive ions generated in the electron stream are formed into a “ribbon-like” beam and ejected into the magnetic field through a narrow slit in the base of the ionisation chamber. In this field, usually generated by a permanent magnet, they are bent in circular paths through 180° towards the defining slit in the collector plate. The radius of curvature of paths (R) depends upon (i) the

strength of the magnetic field, (ii) the charge to mass ratio of the ions and (iii) the energy of the ions. For ions of a given charge-to-mass ratio the radius of curvature is directly proportional to the square root of their kinetic energy and inversely proportional to the magnetic field strength. As illustrated in Fig. 1, some ions will have a radius exactly equal to R_0 and reach the collector plate through the collector defining slit. The “heavier” and “lighter” ions have respectively radii greater or less than R_0 and, hence, fail to reach the collector. The various components of the ion beam can be scanned across the collector defining slit by varying the kinetic energy of the ions (i.e. by controlling the bias voltage V of the ion source).

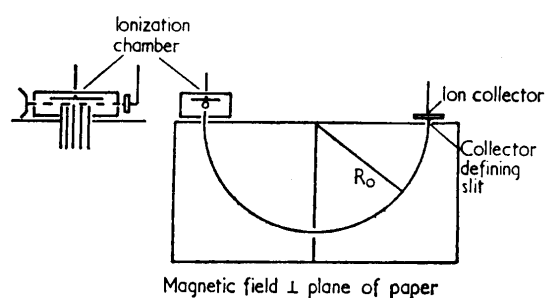


Fig. 1 180° deflection magnetic mass spectrometer.

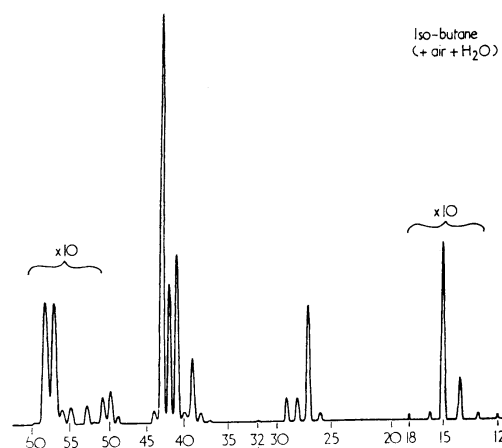


Fig. 2 Typical spectrum for magnetic deflection mass spectrometer showing iso-butane with a small impurity of water vapour and air [1].

Figure 2 depicts a typical spectrum for this instrument. In this diagram the ion current to the collector is plotted as a function of the source bias voltage (i.e. the kinetic energy of the ions). It will be noticed that this method of scanning results in a non-linear display; the value of V being very low for ions of high charge-to-mass ratio. In fact a useful output is obtained with V kept constant and scanning effected by varying the magnetic field strength. Unfortunately the electro-magnets required to generate variable magnetic fields tend to be both bulky and unrealistically expensive for general vacuum use.

An alternative to the magnetic deflection spectrometer is the Omegatron which, unfortunately after extensive development showing promise, has not found significant practical applications. The electrodes of this analyser form a small cube with insulated plates at top and bottom across which a radio frequency potential difference can be applied. This is illustrated in Fig. 3. Positive ions formed in the central electron beam are forced, by the strong magnetic field parallel to this axis, to travel in circular paths, as indicated in Fig. 3. The time of revolution T in the magnetic field is given by

$$T = \frac{2\pi M}{eB}$$

with the usual notation. It is significant that this time is dependent upon the magnetic field strength and the mass of the ions, but not their energy. Thus ions with one particular mass will resonate with the field applied across the RF plates and, therefore, gain energy continuously. The radius of curvature of their paths will increase until they strike the collector. A complete mass spectrum can be obtained by varying either the magnetic field strength or the frequency of the RF signal. Unfortunately, although this instrument is small and easily fitted to a vacuum system, it requires a very strong magnetic field for effective operation. Resolution is inversely proportional to mass in the omegatron; making performance poor at the high end of the spectrum. This does however mean that, although not practical for general use, it could have applications where interest is confined to “light” ions; resolution is certainly excellent in the range 1–4 amu.

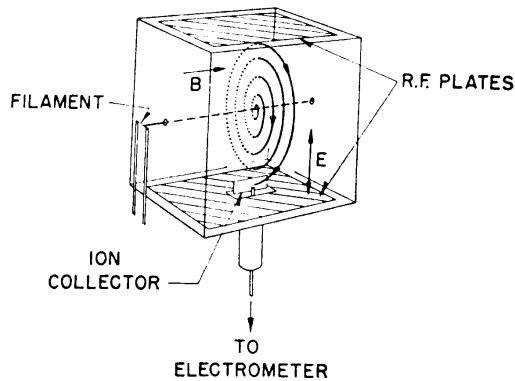


Fig. 3 The Omegatron [2].

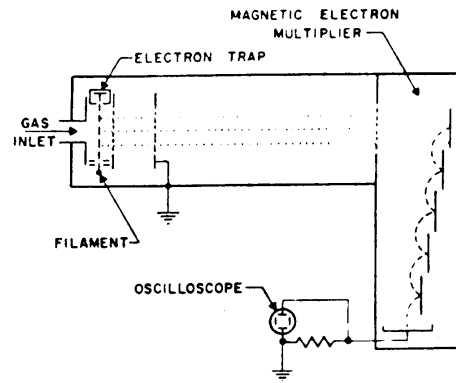


Fig. 4 The time-of-flight mass spectrometer [3].

The time-of-flight mass spectrometer has the advantages of a relatively small size and, more important, does not require any magnetic field for its operation. The principle of operation is simple; ions are formed as a bunch in a pulsed electron beam (say of $1\mu\text{sec.}$ duration). They are all accelerated through the same potential difference (therefore receiving the same kinetic energy) and are constrained to drift in a field-free space to an ion collector, as shown in Fig. 4. Obviously mass separation will occur because light ions, travelling faster, will reach the collector before the heavy ions. With a sensitive multiplier and an amplifier with a small time constant the arrival time of the various ions can be measured and displayed. This instrument gives an intermittent output signal that limits its value. It also has the disadvantage of low sensitivity and should high performance be required a long drift tube must be used, thus negating the advantage of small size. This has inhibited its development for general vacuum use.

For practical operation it has been established that none of the above instruments, with the possible exception of the magnetic deflection mass spectrometers, can mount a serious challenge to the quadrupole mass filter which is now used almost universally in general vacuum application.

2. THE QUADRUPOLE MASS FILTER

In its simplest form this filter (or analyser) can be considered as a conventional extractor ionisation gauge with an electrostatic mass filter interposed between the ion source and the ion collector. The filter takes the form of four parallel rods of circular, or near circular, cross-section mounted symmetrically about a central axis. In a typical instrument for general vacuum use these rods are between 5 and 10-mm diameter and 50 to 150-mm long. Precision in mounting the rods is most important. Opposite rods in the assembly are connected together electrically, the structure being shown schematically in Fig. 5. Ideally the rods must have the hyperbolic profiles illustrated in Figs. 6a and 6b. Practical experience has shown that the actual field is sufficiently close to hyperbolic when circular rods are substituted for those shown in Fig. 6a, provided the radius r of the rods is chosen to be such that $r = 1.147r_0$, r_0 being the inscribed radius shown in Fig. 6b. With a suitable electrical potential applied between the two pairs of rods a filtering action takes place for ions injected from the source along the central axis of this symmetrical structure. The electric field (in the plane at right angles to the z axis of Fig. 6a) must be hyperbolic in order to obtain the best filtering action.

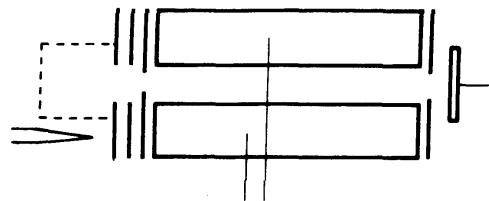


Fig. 5 The quadrupole mass spectrometer.

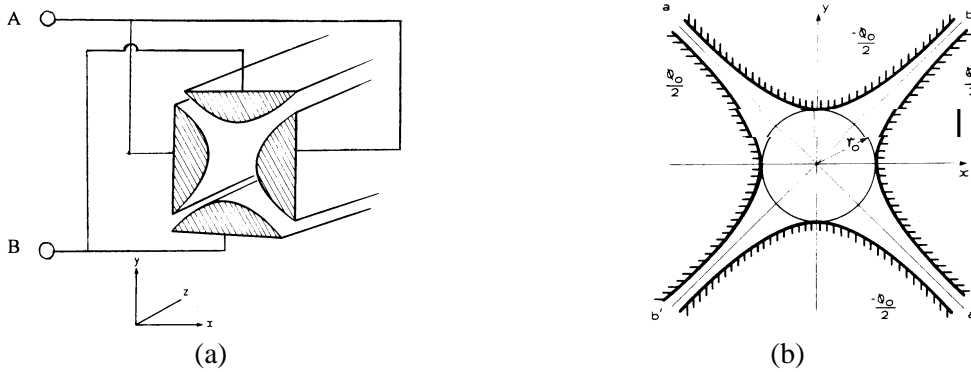


Fig. 6 Rod assembly in quadrupole filter. (a) Showing electrical connections. (b) Defining inscribed radius.

In order to obtain the filtering action an RF voltage superimposed upon a dc voltage must be applied between the two pairs of rods, i.e. a voltage $U + V \sin \omega t$ must be applied between terminals A and B in Fig. 6a. Theory indicates that U , V and ω can be chosen such that, whilst the majority of ions will be unstable in the x or y directions (or both), a small fraction may be stable in both x and y directions and therefore travel the full length of the filter (z direction in Fig. 6a) to reach the collector. The criteria for determining stability can be obtained from the diagram presented in Fig. 7. This maps out the boundaries of stability/instability for what is in effect the (U, V) plane. Because the stability criteria depends upon M , ω and r_0 as well as U, V , Fig. 7 is presented in terms of the more general co-ordinates a and q which are defined as follows:

$$a = \frac{4eU}{m\omega^2 r_0^2} \quad q = \frac{2eV}{m\omega^2 r_0^2}$$

If a point plotted in Fig. 7 for particular values of a and q lies inside the triangle then the ion paths are stable; if a point lies outside the triangle then the paths are unstable. It has to be pointed out that the boundaries of the triangle in Fig. 7 are strictly speaking only correct for very long filters; as basic theory only concerns itself with ions that have exposure to virtually an infinite number of cycles of the RF field. However, Fig. 7 is a sufficiently good approximation provided the ions are subject to more than about 100 cycles of the RF voltage in the filter.

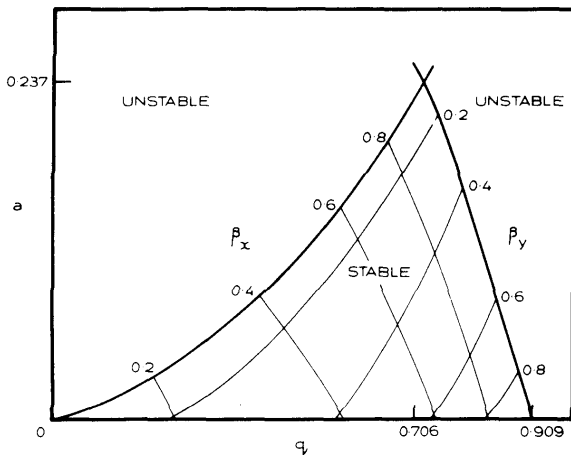


Fig. 7 The first stability zone.

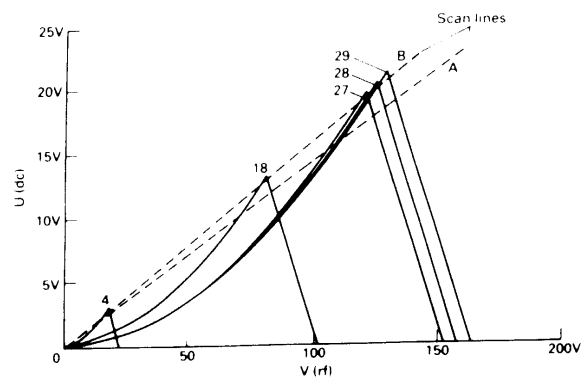


Fig. 8 Stability diagram plotted for singly charged ions of mass 4, 18, 27, 28, & 29 amu [4].

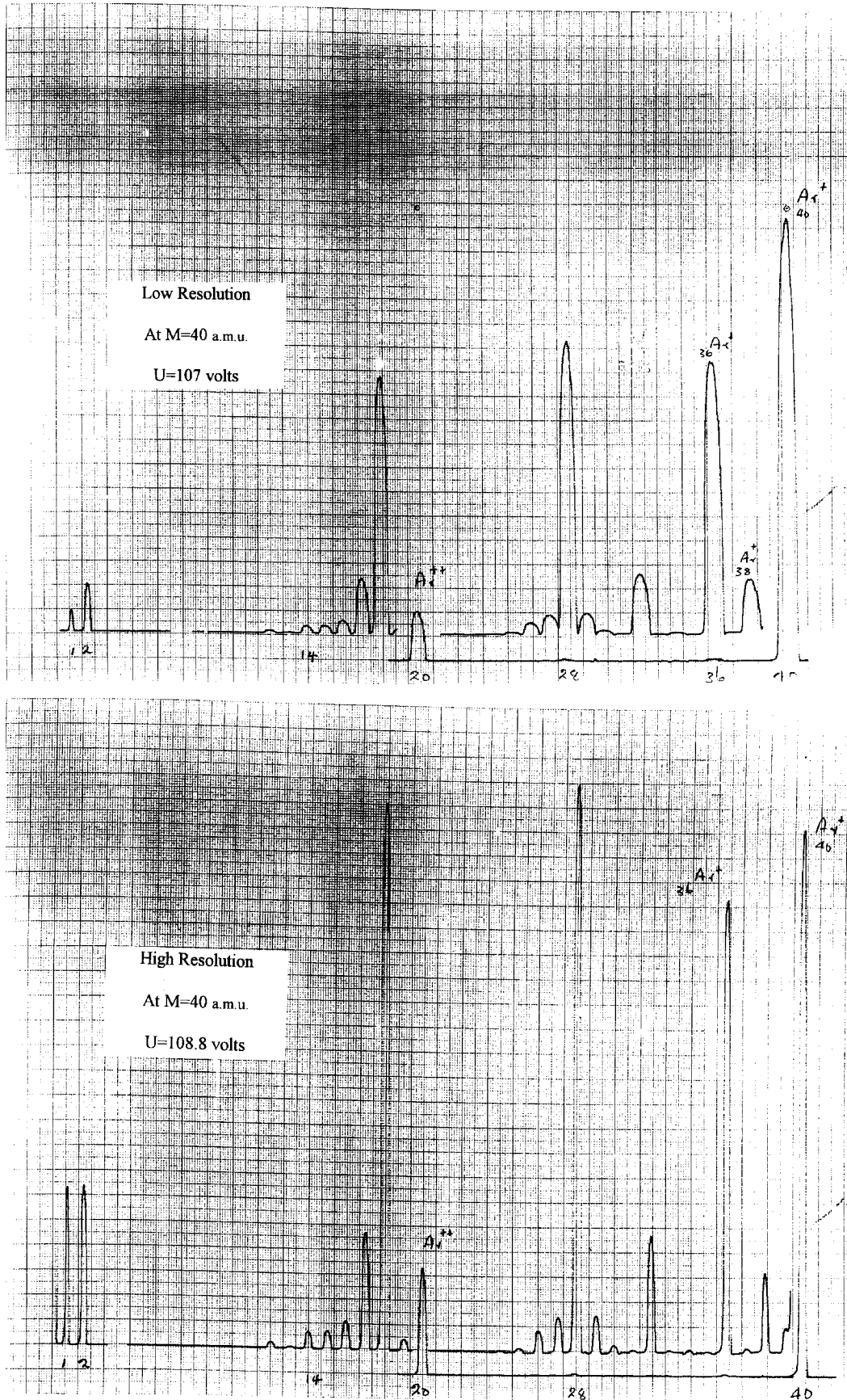


Fig. 9 Mass spectra obtained at both low and high resolution.

The significance of the “stability triangle” is illustrated clearly in Fig. 8. In this figure triangles are drawn in terms of U and V (for fixed values of ω and r_0) for five different values of ion mass M (singly charged ions with mass 4, 18, 27, 28 & 29 a.m.u). These five triangles are computed for an ac frequency of 2 MHz and a rod radius of 3.25 mm. A family of similar triangles is obtained with the tips of the triangles all lying in a straight line that passes through the origin. Obviously mass spectra can be obtained if the applied voltage is increased from zero to a high value, keeping the ratio of U/V constant. Two such “scan lines” are shown in Fig. 8. Obviously by increasing the slope of this line an increase in resolution will be obtained. Corresponding experimental results are given in Figs. 9a and 9b. These two diagrams show clearly how the resolution increases significantly for only a 2% change in the slope of the scan line (i.e. an increase in U at mass 40 amu from 107 to 108.8). The ability to control resolution by a simple adjustment of the electrical parameters is an important advantage of the quadrupole over the magnetic deflection instruments. (In the magnetic instruments resolution can only be changed by physically altering the defining slit widths at source and collector). A further advantage — not immediately obvious — is the requirement of the quadrupole for increased applied voltage levels at the highest masses. This means that, unlike the magnetic deflection spectrometers and the omegatron, the quadrupole is least sensitive to electrode surface contamination at the high mass end of the scale. This is a positive advantage because usually it is at the highest masses where the highest precision is required.

There is good agreement between the experimentally measured performance, as typified by the data presented in Fig. 9, and the theoretical predictions of Figs. 7 and 8. This is true in spite of the small, but numerous, approximations in the mathematical model. For example, as already noted, the ions are subject to only a finite number of cycles of RF field. Also the fact that the ions have to travel through fringing fields to enter and exit the filter is completely ignored in the basic theory. It is also true that there must be some deviations from a true hyperbolic field because (i) the electrode surfaces are almost always circular in section rather than hyperbolic, (ii) there must be some errors in mounting the rod assembly and (iii) there will occasionally be some spurious electrical charge due to insulating layers building up on the electrode surfaces.

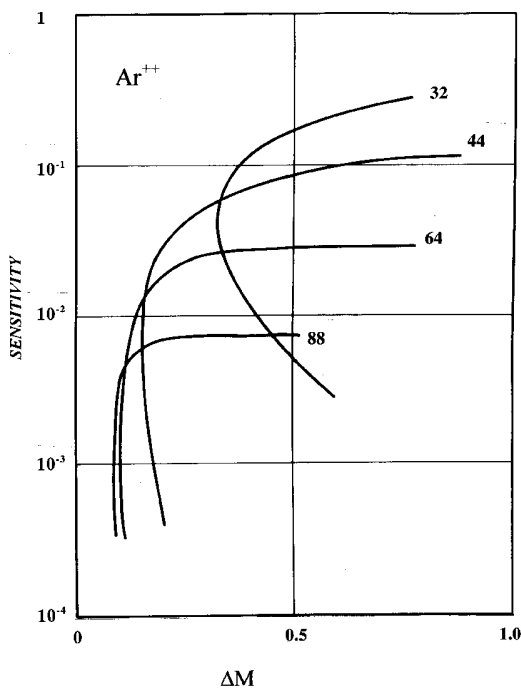


Fig. 10 Experimental results showing relation between sensitivity and resolution for different values of N the number of cycles the ions spend in the filter (the values of N are marked on each curve).

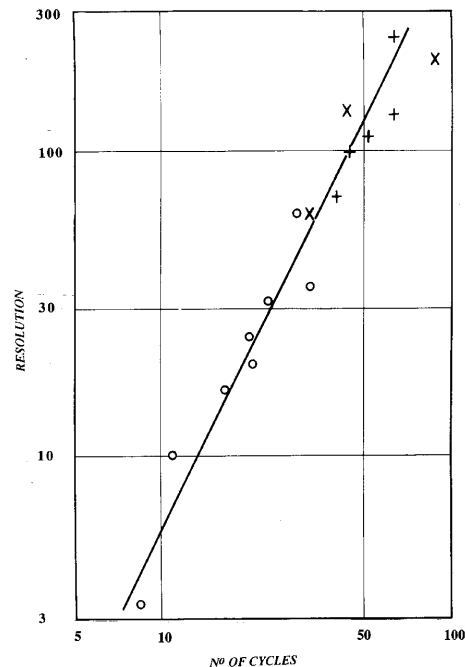


Fig. 11 Relation between maximum resolution and the number of cycles the ions spend in the lens.

From data obtained in experiments of the type depicted in Figs. 9a and 9b families of curves, such as that shown in Fig. 10, can be built up. These demonstrate how sensitivity and resolution depend very much upon N , the number of cycles of RF which the ions “experience” in the filter. In Fig. 10 the number of cycles N is indicated on each curve; thus in this particular filter maximum resolution attainable increases from about 50 to 200 when N is increased from 32 to 88 cycles. Resolution is defined here, and throughout the paper, by the ratio $M/\delta M$ where δM is the peak width at 10% of the peak height. This is conventional.

Figure 11 obtained from many families of curves similar to those in Fig. 10 shows the simple relationship between maximum resolution and number of cycles N over a range of values of ion charge to mass ratio. Although there is considerable scatter in the experimental points (bearing in mind that this is a log-log plot), the relationship between R and N is given by $R = N^n$ where n is close to 2.

3. THE DESIGN OF PRACTICAL QUADRUPOLE FILTERS

The requirements for optimisation of the four important parameters are as follows:

Increase Resolution:

1. Increase length of filter
2. Increase frequency of RF
3. Decrease ion injection energy

Decrease cost

1. Decrease frequency of RF
2. Decrease length of filter

Increase sensitivity

1. Increase ion injection energy
2. Introduce a multiplier at the collector
3. Increase electron current

Increase mass range

1. Reduce frequency
2. Increase the ac and dc voltages

Unfortunately there are serious clashes in the requirements, which means that compromises are necessary in virtually all designs. For example a decision to increase the resolution of a given filter by increasing either its length or the frequency of the RF supply incurs a cost penalty. The manufacture of a long filter is obviously more expensive than a short filter (also it can be less convenient to attach to a vacuum system). An increase in RF frequency leads to an increased requirement from the ac and dc voltages (U and V). This means more expensive and larger power supplies. Increasing resolution by reducing the speed with which the ions travel through the filter in the z direction (i.e. by reducing their injection energy) appears attractive but, unfortunately, a lower sensitivity must be accepted. This might be compensated by introducing an electron multiplier into the collector assembly as shown in Fig. 12. Again there is a cost penalty.

Stability of performance over a long period, a factor of considerable practical importance, is difficult to quantify. It is well established that stability depends significantly upon the energy with which the ions are injected into the filter. Obviously changes in the performance of the instrument with time depend critically upon the atmosphere in the vacuum system. Whilst in ultra-high vacuum systems instability will probably not be a problem it can be significant even in relatively clean, but unbaked, systems.

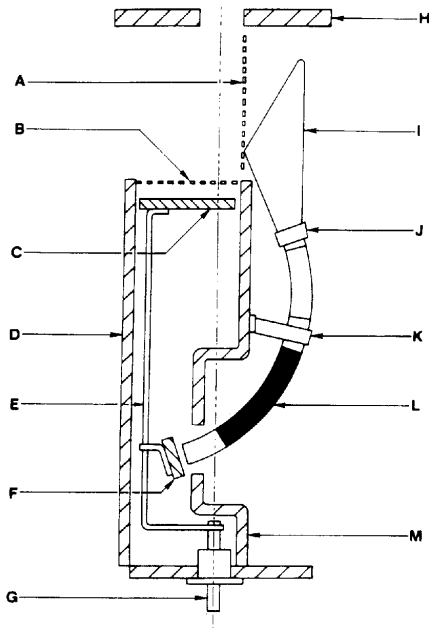


Fig. 12 Channel electron multiplier connected to quadrupole exit plate H. A, high-voltage; B, grounded mesh; C, ion collector; D, grounded shield; E, signal lead; F, electron collector; G, output connector; I, CEM cone; J, high-voltage connection; K, ground connection; L, bias resistor; and M, grounded shield, [5].

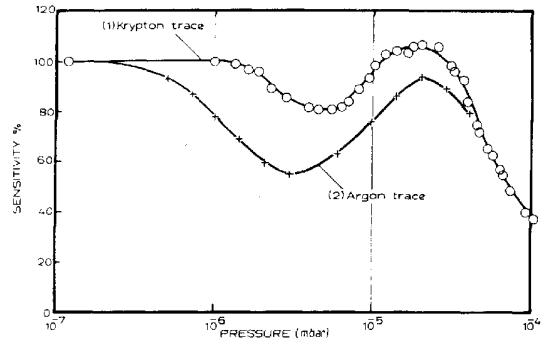


Fig. 13 Observed variation in sensitivity over the pressure range 10^{-7} to 10^{-4} mbar for a residual gas analyser [6].

Since space charge fields, both negative and positive, can be more important in the mass filter than in the ionisation gauge it is important to recognise that (i) because of the negative space charge the sensitivity, i.e. (output current)/(partial pressure) is not necessarily proportional to electron current and (ii) because of positive space charge, sensitivity is not necessarily independent of pressure even when mean-free-path effects can be neglected. The magnitude of the non-linearity depends very much upon individual instrument design.

A simple technique for measuring non-linearity in the output vs pressure characteristics is illustrated in Fig.13. This presents the data obtained from two sets of measurements obtained with a dynamic calibration plant where two gases were introduced under controlled conditions through separate inlet valves Ref. [6]. In one experiment a flow of argon was first introduced so as to maintain a constant partial pressure of the order of 10^{-8} mb then krypton was introduced at a steadily increasing rate, taking the total pressure in the system from below 10^{-7} mb to about 10^{-4} mb. The variation in the indicated partial pressure for argon demonstrates the change in sensitivity for argon over this pressure range 10^{-7} mb to 10^{-4} mb. For completeness the experiment has been repeated with the two gases reversed, i.e. krypton now becoming the trace gas. Both sets of results indicate a significant dip in sensitivity at comparatively low pressures, where effects of mean free path can be neglected. This experiment indicates the need for caution in interpreting data from these instruments, because the instabilities in the signals from the trace gas could erroneously be interpreted as a fall in pressure for these gases.

4. THE FOUR OPERATING ZONES FOR THE QUADRUPOLE FILTER

All references to theoretical analysis and experimental data in the above sections refer to the filter in the "first operating zone". Extending the analysis from the very brief presentation above shows clearly the existence of a number of additional stability zones; which may well have practical significance.

Meaningful theoretical analysis is based upon a solution of the Mathieu equation which defines stability in both the x and y directions. Analysis and its interpretation is simplified because motion in the x , y and z directions (x , y and z as defined in Fig. 6) is uncoupled and, therefore, the ion motion in

these three directions including the conditions for stability can be considered independently. Further the z direction can be discounted as the electric field in this direction is, in theory, always zero. Thus from the analysis point of view this filter presents a two dimensional problem, with displacements as a function of time in the xz and yz planes being the defining factors. Results of the analysis of the Mathieu equation show clearly defined stability zones in the aq diagram for motion in the xz and yz planes. These zones are shown for a relatively large range of a and q for motion in the xz plane (Fig. 14).

Stability in the yz plane is obtained by reversing the a axis, i.e. $+a$ becoming $-a$ and vice-versa. Figure 15 presents the stability characteristics for both the xz and yz planes superimposed in one diagram. It shows four regions where motion is stable in both planes. These are regions where ions will be able to pass through the filter. The first stability region (the region depicted in Fig. 7) is the small triangle near the central origin, difficult to distinguish in this larger scale diagram.

Although operation in the second and higher stability zones have been neglected in the past, there is now indication of an interest in developing filters for operation in zone III of Fig. 15.

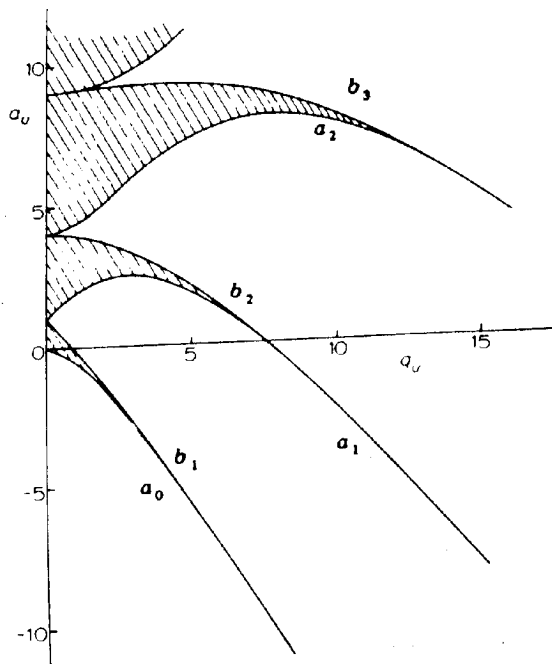


Fig. 14 Stability diagram for the Mathieu equation for either the xz or yz directions.

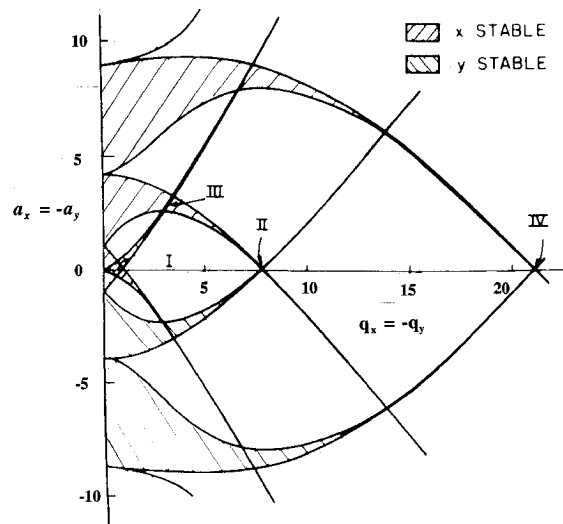


Fig. 15 Stability shown for both xz and yz planes indicating four regions where ions may pass through the filter.

5. REFERENCES

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