

Residual Gas Analyzers

Residual gas analyzers have become so common that almost every vacuum technologist has seen one in the laboratory or attached to an occasionally troublesome system on the manufacturing line. In 1960 Caswell [1] used the RGA to study the residual gases in vacuum evaporators and demonstrated that the performance of a conventional system could be improved by Viton gaskets, Meissner traps, and getters. For thin-film deposition the importance of thoroughly outgassing the source material was stressed. Caswell also used the RGA to study the effects of residual gases on the properties of tin and indium films [2,3]. Since that time the instrument has proved its value in the solution of device fabrication problems by measuring other properties such as gas purity, gas loads evolved from films, and background gas composition during sputtering and other plasma processes.

This chapter is concerned with the theory of the operation of magnetic sectors and RF quadrupoles and the methods of installation of and data collection on vacuum and sputtering chambers. The interpretation of data is discussed in Chapter 9.

8.1 INSTRUMENT DESCRIPTION

RGAs and mass spectrometers are used to measure the ratio of mass to electric charge of a molecule or atom. First the molecules are ionized, then directed through a mass separator, and finally detected. See Fig. 8.1. A variety of methods has been developed for each of the three stages of particle identification. Some approaches are sophisticated and are applicable to analytical laboratory mass spectrometers that are capable of differentiating small fractional mass differences; for example,

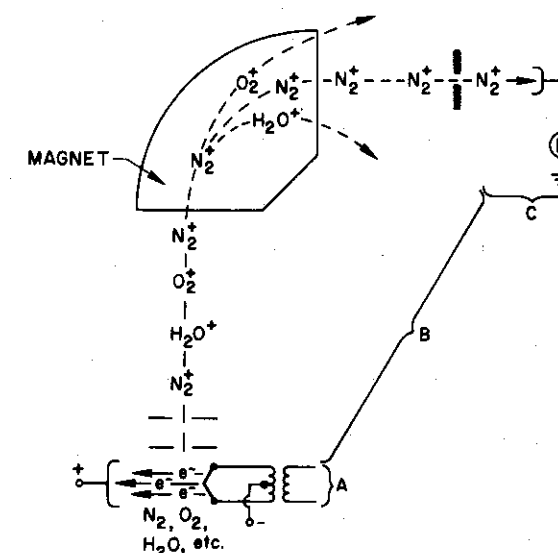


Fig. 8.1 Three stages of partial pressure analysis: (a) Ionization—hot filament illustrated; (b) mass separation—magnetic sector illustrated; and (c) detection—Faraday cup illustrated.

carbon monoxide ions ($M = 27.9949$ AMU) and molecular nitrogen ions ($M = 28.0061$ AMU) are easily separable on a double-focusing magnetic sector. (The weight of ¹²C is 12 AMU.) Other methods have been developed into portable instruments that scan the mass range 1 to 50 AMU or perhaps 1 to 300 AMU and are able to resolve adjacent peaks 1 AMU apart. The latter instruments are collectively referred to as residual gas analyzers. This section reviews briefly the most commonly used ionization, separation, and detection methods in RGAs.

8.1.1 Ionization Sources

Virtually the only technique applicable to the production of positive ions in commercial residual gas analyzers is electron impact ionization. Other techniques such as field ionization and chemical ionization are useful in some research applications. Figure 8.2 is an ionization chamber that might be used in a residual gas analyzer. The electrons from the filament are drawn across the chamber to the anode. While crossing this space some of the electrons collide with gas molecules, strip off one or more of their electrons, and create positive ions. Not all ionization chambers are geometrically similar to the one sketched in Fig. 8.2. One instrument looks very much like a Bayard-Alpert ionization gauge except for the absence of the wire collector and the addition of an electron reflector

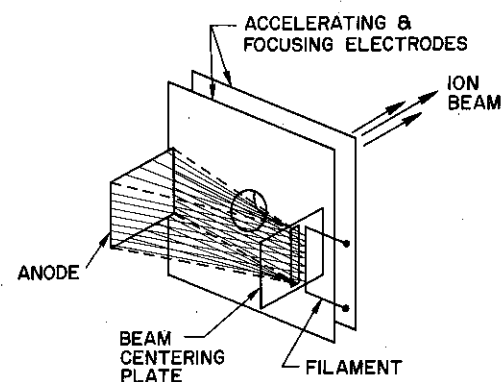


Fig. 8.2 One form of an ionizing source used in a residual gas analyzer.

outside the filament. These and other ionizers were designed to maximize ion production and instrument sensitivity.

As in the ion gauge, positive ion production is not the same for all gases. The RGA differs from the ion gauge in that it sorts ions by their mass-to-charge ratio and counts each ratio separately. Thus for nitrogen the ion gauge makes no distinction between a current due to N^+ ($M/z = 14$) or N_2^+ ($M/z = 28$), while the RGA does distinguish the two ion currents. Table 8.1 gives the total positive ion cross sections relative to N_2 for several common gases at an ionizing energy of 70 eV [4]. Although the ionization cross section does not peak at the same energy for all gases, it is generally greatest for most gases somewhere in the 50-to-150-eV range. For this reason most ionizers operate at a potential of 70 V. Some instruments make provision for the adjustment of the ionizing voltage because it is sometimes desirable to reduce the potential in order to reduce the dissociation of complex molecules. This is essential in qualitative analysis.

The ion production of each species is proportional to its density or partial pressure. Consider a sample of a gas mixture containing only equal portions of nitrogen, oxygen and hydrogen whose total pressure is 3×10^{-5} Pa. A mass scan of this mixture would show three main peaks of unequal amplitudes. All other factors being equal, the main oxygen peak would be slightly larger and the hydrogen peak about half as large as the nitrogen peak because of differences in relative sensitivity or ionizer yield. If, however, the total pressure of the gas mixture were increased to 6×10^{-5} Pa, the amplitudes of each of the three main peaks would double. In other words, the instrument is linear with pressure. Linearity of the ionizer extends to a maximum total pressure of order 10^{-3} Pa. At higher pressures space charge effects and gas collisions become important. The ions produced in the space between the filament

Table 8.1 Experimental Total Ionization Cross Sections (70 V) for Selected Gases Normalized to Nitrogen

Gas	Relative Cross Section
H ₂	0.42
He	0.14
CH ₄	1.57
Ne	0.22
N ₂	1.00
CO	1.07
C ₂ H ₄	2.44
NO	1.25
O ₂	1.02
Ar	1.19
CO ₂	1.36
N ₂ O	1.48
Kr	1.81
Xe	2.20
SF ₆	2.42

Source. Reprinted with permission from *J. Chem. Phys.*, 43, p. 1464, D. Rapp and P. Englander-Golden. Copyright 1965, The American Institute of Physics.

and anode are drawn out of that region, focused, and accelerated toward the mass separation stage. The acceleration energy depends on the type of mass analyzer that follows, and in a magnetic sector instrument ion acceleration is really a part of the mass separation stage.

8.1.2 Mass Separation

Almost a dozen techniques have been developed for mass separation of ions generated by a method like the one just described. For various reasons only two techniques, the magnetic sector and the RF quadrupole, have survived the test of widespread commercial development. Those who are interested in a thorough discussion of all types of mass separation schemes are referred to other sources [5]. The common methods are outlined in Fig. 8.3. This section discusses the quadrupole and magnetic

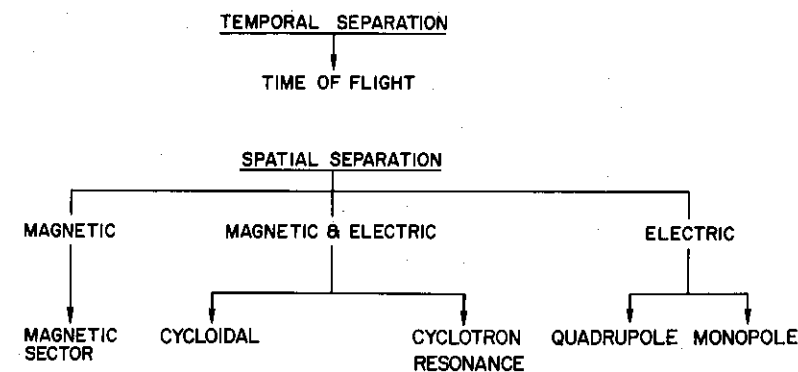


Fig. 8.3 Mass separation methods.

sector mass separation methods as they are commonly used in residual gas analyzers.

Magnetic Sector

The magnetic sector analyzer, which was developed 60 years ago [6], separates ions of different mass-to-charge ratios by first accelerating the ions through a potential V_a and then directing them into a uniform magnetic field perpendicular to the direction of the ion motion. While under the influence of this magnetic field the ions are deflected in circular orbits of radii r given by

$$r = \frac{1}{B} \left(\frac{2mV_a}{ze} \right)^{1/2} \quad \text{▶ (8.1)}$$

If B is given in units of teslas, the ion accelerating energy V_a , in volts, the mass M , in mass units, and z is the degree of ionization, the radius of curvature will be

$$r = \frac{1.44 \times 10^{-4}}{B} \left(\frac{MV_a}{z} \right)^{1/2} \quad \text{(8.2)}$$

A practical mass analyzer that uses magnetic separation is shown in Fig. 8.4 for a 60° magnetic sector. In principle, any angle will work, but angles of 180° , 90° , and 60° are common. The 60° sector is a common filter for RGA applications. It provides sufficient separation between source and collector, and good focusing for divergent ions and requires a minimum amount of magnetic material.

As illustrated in Fig. 8.4, the location of the exit and entrance slits determine the radius r at which the beam will be properly focused. With

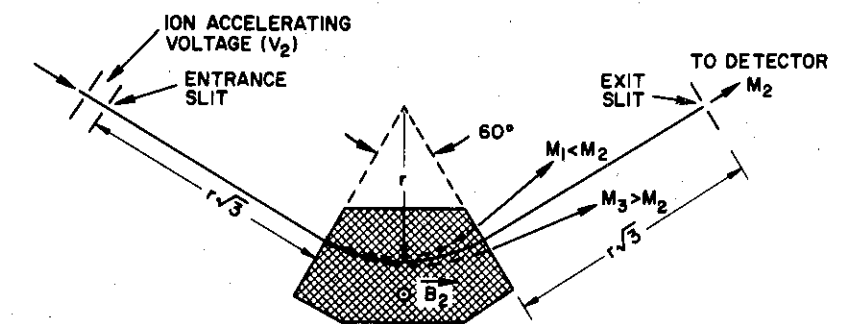


Fig. 8.4 A magnetic sector mass separator (60°) with symmetrical entrance and exit slits. Adapted with permission from *Mass Spectroscopy in Science and Technology*, p. 18, F. A. White. Copyright 1968, John Wiley & Sons.

the radius so specified, the mass-to-charge ratio M/z of the beam in focus is determined by the accelerating potential and the magnetic field strength. In the example shown a singly ionized molecule $z = 1$ of mass M_2 is focused on the exit slit for $V_a = V_2$ and $B = B_2$. Masses $M_1 < M_2$ and $M_3 > M_2$ will be deflected through greater and lesser angles, respectively, than M_2 . To focus mass M_3 on the detector, B must be increased or V_a must be decreased. Commercial RGAs generally use permanent magnets and a variable acceleration voltage. Electromagnets are available to extend the range and provide magnetic scanning.

Equation (8.1) states that for constant r and B , the quantity MV_a/z is a constant. From this it can be seen that sweeping a large mass range, say, $1 \leq M \leq 300$, requires prohibitively large linear sweep voltages. Because of this limitation, permanent magnetic sector analyzers divide the instrument range into at least two scales by changing the magnet; for example, one scale might cover the mass range $2 \leq M < 50$ with a magnet of about 0.1 T and a second mass range of $12 \leq M \leq 300$ with a magnet of 0.25 T. Traditionally, but not exclusively, such instruments sweep the voltage linearly with time. Because MV_a/z is a constant, the resulting mass scan is not linear with time; as the mass number increases, the peak separation decreases. Somewhat more expensive instruments allow the accelerating potential to be held constant while an electromagnet of 0 to 0.25 T sweeps the range $1 \leq M \leq 100$.

Differentiation of (8.1) reveals that the mass dispersion Δx of the instrument is mass dependent. For ions of equal energy traversing a uniform magnetic sector the mass dispersion, or spatial separation between adjacent peaks of mass m and $m + 1$, has been found to be [5]

$$\Delta x \propto \frac{r}{m} \quad \text{▶ (8.3)}$$

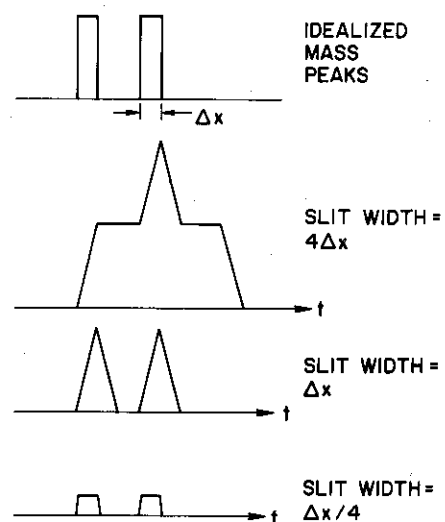


Fig. 8.5 Idealized mass peaks illustrate the trade-off between sensitivity and resolution.

Equation (8.3) illustrates why instruments of small radii cannot effectively separate adjacent heavy mass peaks. The resolution and sensitivity of a magnetic sector are dependent on mass and exit slit width.

Figure 8.5 shows two idealized mass peaks being scanned with slits of different widths and indicates that wide slits are efficient collectors of ions (high sensitivity) but poor resolvers of adjacent mass peaks (low resolving power). To first order there are no mass dependent transmission losses in a fixed-radius, magnetic sector instrument. This means that if equal numbers of, say, hydrogen and xenon molecules pass through the entrance slit, equal numbers will pass through the exit slit. It will be noted later that this is not always true of the quadrupole. Figure 8.6 shows an RGA trace taken with a small sector instrument [7] on a 35-in. oil diffusion pumped system. This trace clearly illustrates the non-linear nature of the sweep and the mass dependent resolution. Because the slit width at the detector is fixed and the distance between adjacent mass peaks varies as $1/m$, the valley between two peaks of unit mass difference is not so pronounced at high mass numbers as at low mass numbers. Figure 8.7 was taken on an instrument in which the magnetic field was varied to produce a linear scan. The same kind of mass dependent resolution is also evident here. More detailed discussions of magnetic sectors are found in a number of texts [8,9].

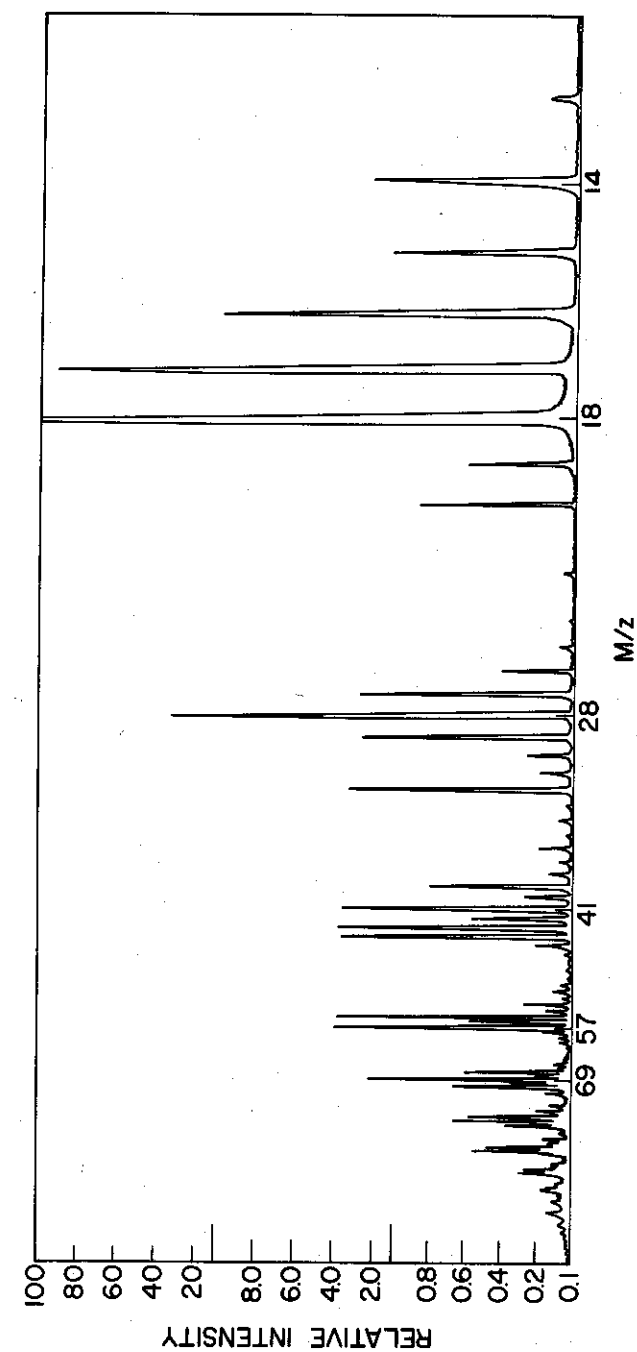


Fig. 8.6 Mass scan from a large diffusion pumped evaporator taken with a magnetic sector instrument with a permanent magnet and voltage sweep.

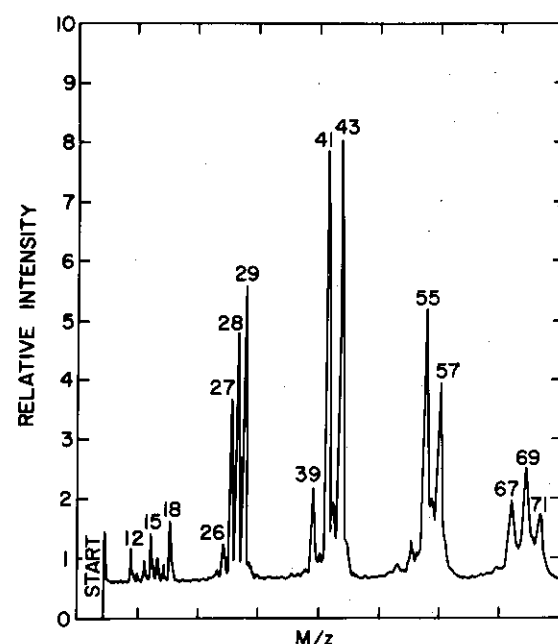


Fig. 8.7 Linear mass scan taken with an Aero Vac 700 series magnetic sector instrument. Reprinted with permission from High Voltage Engineering Corp., Burlington, MA.

RF Quadrupole

The RF quadrupole, developed by Paul [10] and co-workers, is the most popular non-magnetic mass filter in modern RGAs. Its acceptance has been due, in part, to the development of the necessary stable, high power quadrupole power supplies. Figure 8.8 illustrates the mass filter geometry and the path of a filtered ion. The ideal electrodes are hyperbolic in cross section. In practice they are realized by four rods of cylindrical cross section located to provide the optimum approximation to the hyperbolic fields. Each of the rods is spaced a distance r_0 from the central axis. Mosharrafa [11] has provided a non-mathematical explanation of quadrupole operation. The two rods with positive dc potential, $+U$ in Fig. 8.9, create a potential valley near the axis in which positive ions are conditionally stable. The potential is zero along the axis of symmetry, shown in the dotted curve of Fig. 8.9. This field is zero only if the potential $-V$ is simultaneously applied to the other pair of quadrupole rods. It is a property of a quadrupole, not a dipole, field. The addition of an RF field of magnitude greater than the dc field ($U + V \cos \omega t$) creates a situation in which positive ions are on a potential "hill" for a small portion of the cycle. Heavy ions have too much inertia to be

affected by this short period of instability, but light ions are quickly collected by the rods after a few cycles. The lighter the ion, the fewer number of cycles required before ejection from the stable region. This rod pair acts as a "high pass" filter.

The rod pair with the negative dc potential $-U$ creates a potential "hill" that is unstable for positive ions. However, the addition of the RF field creates a field $-(U + V \cos \omega t)$ which allows a potential "valley" to exist along the axis of the quadrupole for a small portion of the cycle provided $V > U$. In this field light ions are conditionally stable and heavy ions drift toward the electrodes because the potential hill exists for most of the cycle. This half of the quadrupole forms a "low pass" filter.

Together the high and low pass filters form a band pass filter that allows ions of a particular mass range to go through a large number of stable, periodic oscillations while traveling in the z -direction. The width of the pass band, or resolution, is a function of the ratio of dc to RF potential amplitudes U/V , while the "sharpness" of the pass band is determined by the electrode uniformity, electrical stability, and ion entrance velocity and angle. A detector is mounted on the z -axis at the filter's exit to count the transmitted ions. Ions of all other M/z ratios will follow unstable orbits and be collected by the rods before exiting the filter. The stability limits for a particular M/z ratio are determined from the solutions of the equations of motion of an ion through the combined RF and dc fields and involve ratios of ω , M/z , r_0^2 and the potentials U and V . A thorough discussion of the RF quadrupole has been given by Dawson [12]. By sweeping the RF and dc potentials linearly in time the instrument can be made to scan a mass range. Scan times as slow as 10

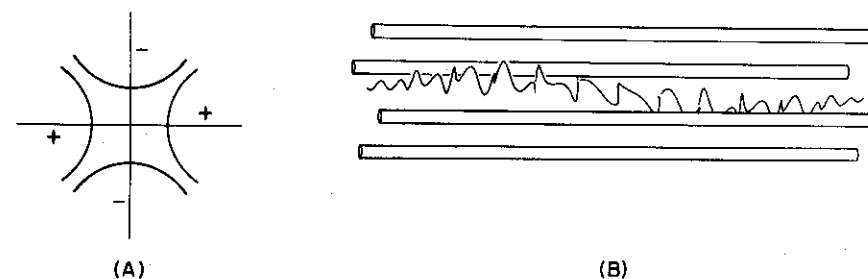


Fig. 8.8 Quadrupole mass filter: (a) idealized hyperbolic electrode cross section; (b) three-dimensional computer-generated representation of a stable ion path. Courtesy of A. Appel, IBM T. J. Watson Research Center.

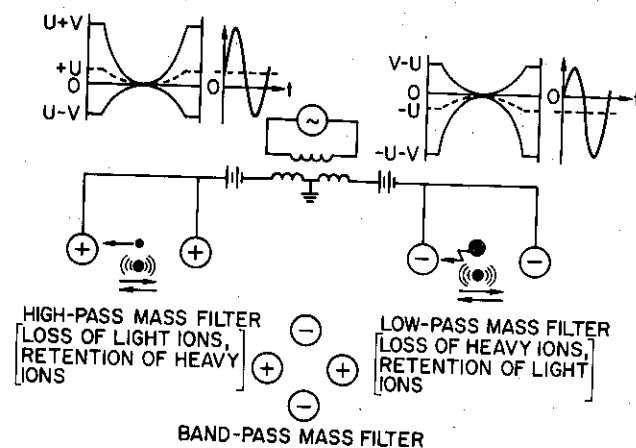


Fig. 8.9 Electric fields in a quadrupole mass filter. Reprinted with permission from *Industrial Research/Development* (March 1970), p. 24, M. Mosharrafa. Copyright 1970, Technical Publishing Co.

to 20 min and as fast as 80 ms are typically attainable in commercial instruments with a range of $1 \leq M/z \leq 300$. One noticeable distinguishing feature of the quadrupole is that no additional restriction other than linear sweeping of the RF and dc potentials is needed to obtain a graphical display that is linear in mass scan.

Although the stability of the trajectory of an ion may be calculated without consideration of the z -component of the ion velocity or the beam divergence, experimentally the situation is more complicated. There is a reasonable range of velocities and entrance angles that does yield stable trajectories. In the magnetic sector both the ion energy and the magnetic field determine the focus point of an ion. One of the advantages of the quadrupole is that ions with a range of energies or entrance velocities will focus even though not with the same resolution. The slow ions are resident in the filter for a longer time and therefore are subjected to a greater number of oscillations in the RF field than are those ions with larger z -components of velocity. As a result the slow ions are more finely resolved but suffer more transmission losses than the light ions. For this reason quadrupole transmission usually decreases with increasing mass. In a typical instrument adjusted for unity resolution the gain is constant to about $20 < M/z < 50$, after which it decays at the rate of approximately a decade per 150 AMU. See Fig. 8.10. This is only typical; there is considerable instrumental and manufacturer variation. By proper choice of the potentials U and V the mass dependence of the transmission can be considerably improved at the expense of resolution. Experimentally mass independent transmission can be achieved by adjusting the sensitivity for two gases, say, argon and xenon, to be the same. If accu-

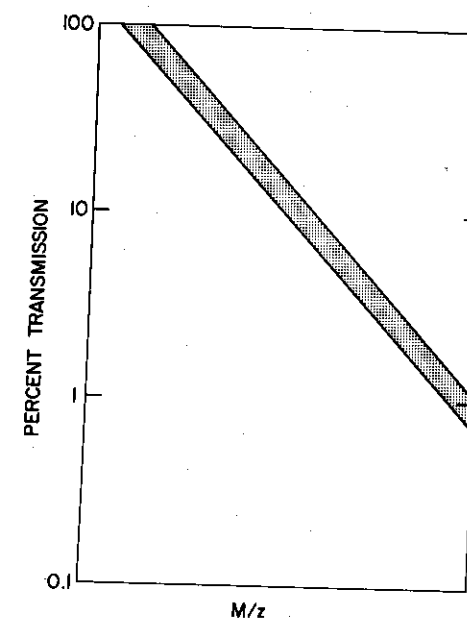


Fig. 8.10 Relative transmission of a typical RF quadrupole as a function of charge-to-mass ratio when adjusted for unity absolute resolution. This may be varied by changing the sensitivity.

rate knowledge of the transmission versus mass is desired, it must be measured for the particular filter and potentials in question. A typical mass scan taken on a small oil diffusion pumped system with a quadrupole adjusted for constant absolute resolution is displayed in Fig. 8.11.

Resolution and Resolving Power

The absolute resolution of an RGA is a measure of the ion-separating ability of the instrument of a given mass M and is given by the peak width ΔM . The American Vacuum Society's tentative standard for absolute resolution [13] specifies that the peak width shall be measured at a point equal to 10% of the peak height. See Fig. 8.12a. The resolving power of an RGA is the ratio of mass to resolution, $M/\Delta M$. In addition to the AVS definition of ΔM , Fig. 8.12 provides some other common definitions. It is evident that the numerical value of the resolving power of a given instrument will vary with the definition. A difference of a factor of 2 in numerical values between these definitions is not uncommon.

The reason that myriad definitions exist is partly historical and partly because no one definition seems to be suitable for all situations. Defini-

tion (b) in Fig. 8.12 is acceptable for two peaks of equal size but does not cover the trace peak next to a main peak. Definition (c) in the same figure is adequate for peaks of unequal magnitude, while definitions (a) and (d) do not require adjacent mass peaks to compute resolving power. In RGA work it is necessary to resolve adjacent peaks separated by one mass unit so that the minimum absolute resolution needed is unity. Analytical spectroscopy necessitates the discrimination of mass peaks separated by small fractional mass units. According to definition (b) in Fig. 8.12 a resolving power of 2000 is needed to distinguish $^{32}\text{S}^+$ ($M/z = 31.9720$) from $^{16}\text{O}_2^+$ ($M/z = 31.9898$). One important aspect of the definitions of resolving power and resolution has not been adequately emphasized; that is, the definitions are incomplete unless the sensitivity is specified. See (8.4). As illustrated in Fig. 8.5, the sensitivity and resolution of a magnetic sector vary with the slit width, while the same parameters are electronically controlled in the RF quadrupole. Because the resolving power can be adjusted over a wide range at the expense of sensitivity, it is misleading to quote the value of only one parameter.

8.1.3 Detection

The ion current detector located at the exit of the mass filter stage must be sensitive to small ion fluxes. The ion current at mass n is related to

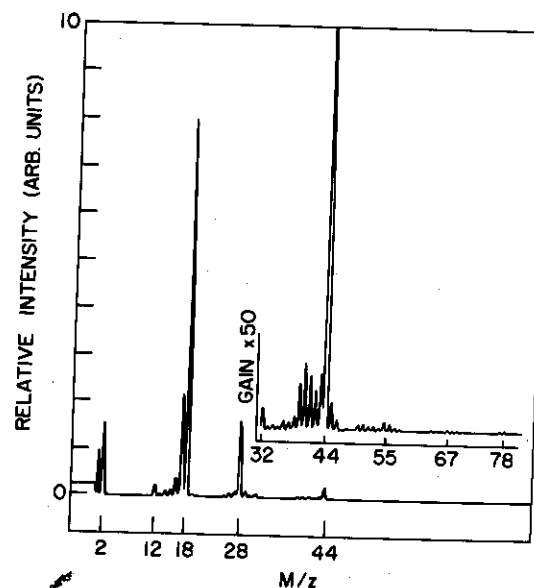


Fig. 8.11 Mass scan taken on a small oil diffusion pumped chamber with an RF quadrupole instrument.

8.1 INSTRUMENT DESCRIPTION

the pressure in the linear region by

$$i_n = S'_n P_n \quad (8.4)$$

where i_n , S'_n , and P_n are, respectively, the ion current, sensitivity of the ionizer and filter, and partial pressure of the n th gas. A typical sensitivity for nitrogen is 5×10^{-6} A/Pa to 2×10^{-5} A/Pa. We might ask why the sensitivity is defined with dimensions of current per unit pressure instead of reciprocal pressure as in ion gauge tubes. The answer is that the ion sources used in RGAs are sometimes space charge controlled, and their ion current is not linearly proportional to their emission current. Some instruments with high sensitivity use very high emission currents, up to 50 mA, but a typical ionizer with a nitrogen sensitivity of 7×10^{-6} A/Pa will have an emission current of 1 to 5 mA. For an emission current of 1 mA the sensitivity, defined as an ion gauge, would be 7×10^{-3} Pa $^{-1}$, which is an order of magnitude smaller than that of an ion gauge. The design of the mass analyzer is responsible for the low "ion

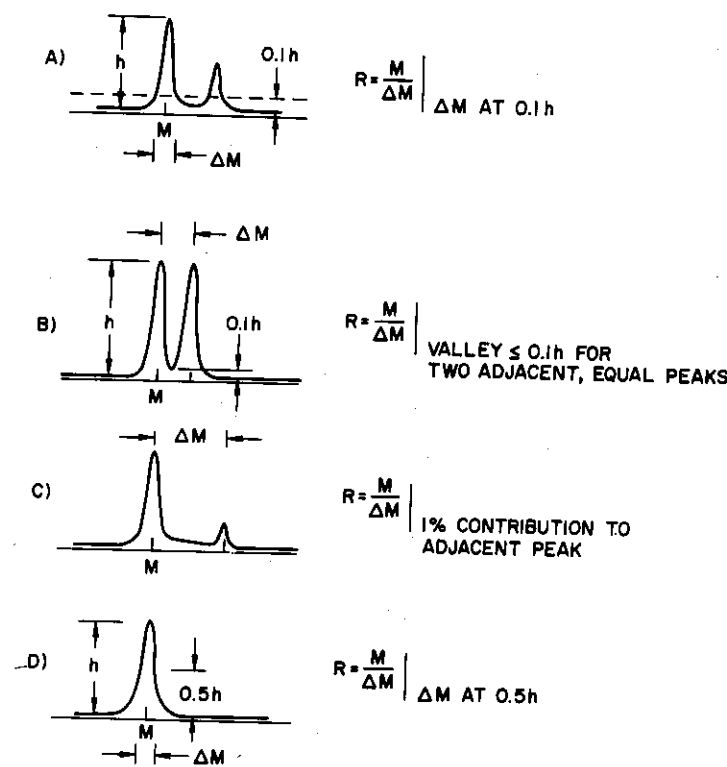


Fig. 8.12 Four definitions of resolving power.