The resolution of a single focusing mass spectrometer is limited by the initial kinetic energy spread of the sample molecules. This spread is minimized in a double focusing instrument by accelerating the sample ions through an electrostatic analyzer, which limits the range of kinetic energies of ions being introduced into the magnetic analyzer. Significantly narrow peaks result.

Resolution = \( \frac{m}{\Delta m} \) (Equation 20-3)

(a) \( \frac{m}{\Delta m} = 28.0(28.0187 - 28.0061) = 2.22 \times 10^3 \)

(b) \( \frac{m}{\Delta m} = 28.0(28.0313 - 27.9949) = 769 \)

(c) \( \frac{m}{\Delta m} = 85.1(85.0653 - 85.0641) = 7.09 \times 10^4 \)

(d) \( \frac{m}{\Delta m} = \frac{115.9}{(232.03800/2) - 115.90219} = 992 \)

(a) In Table 20-3 (page 505), we find that for every 100\(^{79}\)Br atoms there are 98 \(^{81}\)Br atoms. Because the compound in question has two atoms of bromine,

\[
\frac{(M + 2)^*}{M^*} = 2 \times 98/100 = 1.96
\]

and

\[
\frac{(M + 4)^*}{M^*} = \left(\frac{98}{100}\right)^2 = 0.96
\]

(b) Table 20-3 reveals that for every 100 \(^{35}\)Cl atoms, there are 32.5 \(^{37}\)Cl atoms. Thus,

\[
\frac{(M + 1)^*}{M^*} = \left(1 \times \frac{98}{100}\right) + \left(1 \times \frac{32.5}{100}\right) = 1.30
\]

\[
\frac{(M + 4)^*}{M^*} = \left(1 \times \frac{98}{100}\right) \left(1 \times \frac{32.5}{100}\right) = 0.32
\]

(c) \( \frac{(M + 2)^*}{M^*} = 2 \times 32.5/100 = 0.65 \)

\[
\frac{(M + 4)^*}{M^*} = \left(\frac{32.5}{100}\right)^2 = 0.106
\]
20-12 (a)

From detector $R_m$ $R_{in}$ $V_{out}$

$R_m$ should be at least 100 times $R_{in}$. Setting $R_{out}/R_{in} = 100$ will provide the desired voltage gain. If the previous conditions cannot be satisfied it will be necessary to build a voltage follower with gain or a two op amp circuit which uses a voltage follower by a multiplier (see below).

(b)

From detector $R_{in}$ $V_{out}$

A current to voltage converter with gain could be used to produce the same $V_{out}$ but the two op amp circuit better illustrates the processes.

20-13 (a) Because all conditions, except accelerating voltage are constant, Equation 20-9 can be abbreviated to $(m/z)_s = K/V_x$ where $K$ is a constant. Therefore, we can write

$$(m/z)_s = \frac{K}{V_x} \quad \text{and} \quad (m/z)_u = \frac{K}{V_u}$$

The subscripts designate standard (s) and unknown (u). Dividing one of these equations by the other gives the desired relationship.

$$\frac{(m/z)_s}{(m/z)_u} = \frac{K/V_x}{K/V_u} = \frac{V_x}{V_u}$$

(b)

$$\frac{69.00}{(m/z)_u} = 0.965035$$

$$\frac{(m/z)_u}{(m/z)_s} = 21.50$$
(c) The approximately half-integral (m/z) value suggests that the ion being studied in part (b) was doubly charged. This conclusion is in agreement with the fact that the molecular weight of the unknown is 143. The second conclusion is that the unknown must contain an odd number of nitrogen atoms (Nitrogen rule).

20-14 The difference in mass between $^{12}$C and $^{13}$C is 1.00335. Therefore, making the assumption that (P + 1)$^+$ is due only to $^{13}$C means

$$\frac{\text{mass (P + 1)}}{\text{mass (P)}} = 1.00335$$

In Problem 20-13 the following relationship was derived

$$\frac{(m/z)_a}{(m/z)_b} = \frac{V_a}{V_b}$$

Taking into account the fact that only singly charged ions were specified, and rewriting this equation with P representing the standard (s) and (P + 1) representing the unknown (u), the following result is obtained

$$\frac{m (P)}{m (P + 1)} = \frac{m (P)}{m (P) + 1.00335} = \frac{V (P + 1)}{V (P)}$$

(b) Substituting the voltage ratio into the last equation allows $m (P)$ to be calculated.

$$\frac{m (P)}{m (P) + 1.00335} = \frac{V (P + 1)}{V (P)} = 0.987753$$

$$m (P) = 80.92$$

20-15 (1) Ions produced in the spark have a very wide range of energy. Inserting a slit between the electrostatic sector and the magnetic sector is an excellent means of restricting the energy spread of the ions entering the magnetic sector. The presence of the electrostatic sector means that the ions entering the magnetic sector will be both energy and direction focused at the detector. (2) Certain pairs of ions have very similar mass-to-charge ratios that can only be distinguished with a high-resolution instrument.

20-16 $m = 131$ due to $^{36}$Cl$_2$CCH$_2^+$, $m = 133$ due to $^{37}$Cl$^{35}$Cl$_2$CCH$_2^+$,

$m = 135$ due to $^{37}$Cl$^{35}$ClCCH$_2^+$, $m = 117$ due to $^{35}$Cl$^{35}$C$^+$,

$m = 119$ due to $^{37}$Cl$^{35}$Cl$^+$, $m = 121$ due to $^{37}$Cl$^{37}$Cl$^+$