CHEM 221

Instrumental Analysis

Problem Set #5 – Solutions

Spring 2005

Chapter 20

20-5 (a) For CH_4^+, $m/z = 16$ and

$$16 = \frac{B^2r^2e}{2\,V} = kB^2 = k(0.126\,T)^2 \qquad \text{(Equation 20 – 9, page 515)}$$

Similarly, for $m/z = 250$

$$250 = kB^2$$

Dividing the second equation by the first leads to

$$\frac{250}{16} = \frac{B^2}{(0.126\,T)^2}$$

$$B = 0.498\,T$$

Thus to scan the range of m/z of 16 to 250, the field strength would be scanned from 0.126 to 0.498 T.

(b) Here, Equation 20-9 takes the form

$$16 = \frac{B^2r^2e}{2\,V} = \frac{k'}{V} = \frac{k'}{3.00\times10^3}$$

At $m/z = 250$

$$250 = k'/V$$

Dividing the second equation by the first gives

$$\frac{16}{250} = \frac{k'/3.00\times10^3}{k'/V} = \frac{V}{3.00\times10^3}$$

or

$$V = 16\times3.00\times10^3/250 = 192\text{ V}$$

Thus, scan from 3000 to 192 V.

20-6 Here

$$m = 10{,}000\frac{\text{g}}{\text{mol}}\times\frac{1\text{ mol}}{6.02\times10^{23}\text{ ions}}\times\frac{1\text{ kg}}{10^3\text{ g}} = 1.66\times10^{-23}\frac{\text{kg}}{\text{ion}}$$

Substituting into Equation 20-9 gives upon rearranging

$$\text{V} = \frac{(0.240)^2(0.127)^2\,1.60\times10^{-19}}{2\times1.66\times10^{-23}} = 4.48\text{ V}$$

20-8 The presence of a negative dc potential in the *yz* plane causes positive ions to move toward the rods where they are annihilated. In the presence of an added ac potential, this movement is inhibited during the positive half of the cycle with the lighter ions being more affected than the heavier ions. Thus the *yz* plane acts as a low-pass filter removing heavier ions (see Figure 11-6b, page 259).

20-9 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.

20-10 Resolution $= m/\Delta m$ (Equation 20-3)

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

(b) $m/\Delta m = 28.0/(28.0313 - 27.9949) = \underline{\underline{769}}$

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

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

Additional Problems

#1. As determined in the previous problem (20-10b), a resolving power of ***769*** is needed in order to just resolve CO^+ and $C_2H_4^+$. Since ^{12}C has a mass of 12.000000 (exactly) and we are given that CO^+ has a mass of 27.9949, we know that ^{16}O has a mass of *15.9949.* Furthermore, since we are given that $C_2H_4^+$ has a mass of 28.0313, so the mass of ^1H is 1.007825. Now we calculate:

$C_{20}H_{40}^+$ - 280.313
$C_{19}H_{36}O^+$ - 280.2766

R = $m/\Delta m$ = 280/0.0364 = ***7,692***

#2. A quadrupole could handle the resolution of CO^+ and $C_2H_4^+$, but a double-focusing instrument would be needed to resolve $C_{20}H_{40}^+$ and $C_{19}H_{36}O^+$.

#3. There are four possible ways to combine the 2 Cl isotopes:

Mass			
70	$^{35}Cl^{35}Cl$	1.00 x 1.00 = 1.00	→ P
72	$^{35}Cl^{37}Cl$	1.00 x *0.33* = 0.33	→ P+2
72	$^{37}Cl^{35}Cl$	0.33 x 1.00 = 0.33	→ P+2
70	$^{37}Cl^{37}Cl$	*0.33* x *0.33* = 0.11	→ P+4

m/z:	70	72	74
% of parent:	*100*	*66*	*11*

#4. Recall that: $\frac{m_{known}}{V_{unknown}} = \frac{m_{unknown}}{V_{known}}$

So: $\frac{218.9856}{0.99463(5000)} = \frac{m_{unknown}}{5000}$

$m_{unknown} = \mathit{220.1679}$

From the table, this is: $\boldsymbol{C_{11}H_{24}O_4}$

#5. Recall that: velocity = $(2Ve/m)^{1/2}$

So: Time = length/velocity = $L(m/(2Ve))^{1/2}$

$t = (250\text{ cm})[(200/6.023 \times 10^{23})/(2(2700\text{ v})(1.60 \times 10^{-12}\text{ erg/v}))]^{1/2}$

$t = 4.90 \times 10^{-5}$ sec = ***49.0 μs***