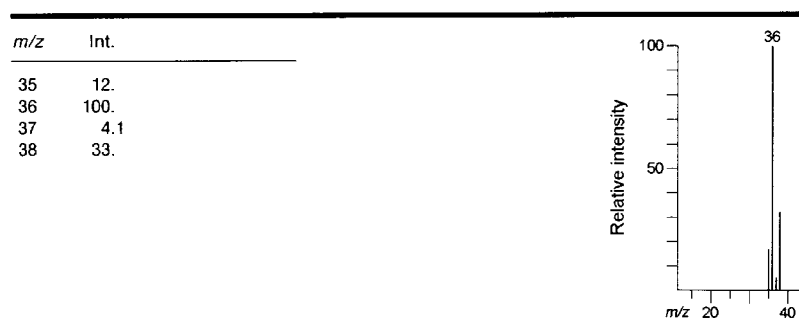


Chemistry 212, Dr. Glaser

Exercise Assignment: Applications of Mass Spectroscopy

The effects of isotopes are illustrated in Unknowns 2.1 to 2.3. The characteristic ratio of 3:1 for Unknown 2.1 makes the element easily recognizable. Note that the interpretation of m/z 36 as a fragment ion would be totally misleading! It is important that you become familiar with the isotope ratios of the common elements.

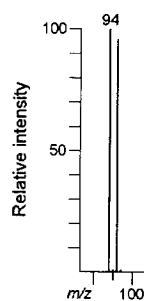
Unknown 2.1



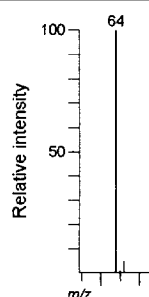
2.1. This spectrum *could* indicate a molecule of mass 38 which could form an abundant fragment ion by the loss of two hydrogen atoms (m/z 36, $[M - 2]^+$). The hints in the text should lead to the observation in Table 2.1 of the 3/1 abundance ratio of the natural chlorine isotopes, masses 35 and 37. Thus, the spectrum is a mixture of $H^{35}Cl$ and $H^{37}Cl$, in proportions corresponding to the isotopic abundances of ^{35}Cl and ^{37}Cl . [Hydrogen chloride]

Unknown 2.2

<i>m/z</i>	Int.
94	100.
95	1.1
96	96.
97	1.1

**Unknown 2.3**

<i>m/z</i>	Int.
64	100.
65	0.9
66	5.0



2.2. The large peaks at masses 94 and 96 should arouse your suspicions; bromine has isotopes of mass 79 and 81 and of nearly equal abundances. Because masses 94 and 96 represent the molecular ions, by difference the molecule contains 15 mass units in addition to the bromine atom; the most logical assignment for this is CH_3 . Peaks at masses 95 and 97 are due to ^{13}C isotopes. [Methyl bromide]

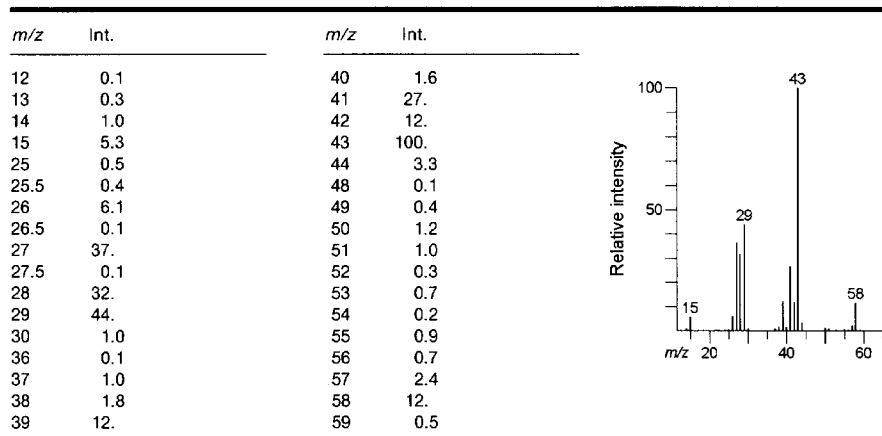
2.3. Look first for the "A + 2" elements. In this case $[m/z\ 66]/[m/z\ 64]$ equals 5.0%; the isotopic-abundance table shows only two elements of such $[(A + 2)^+]/[A^+]$ values, Si (3.4%) and S (4.4%). The former is outside the allowed maximum relative error of 10%. Thus sulfur is indicated, with the ^{33}S abundance of 0.8 agreeing with $[(A + 1)^+]$. Although S_2 would have the correct mass, for this the intensity of the $m/z\ 66$ peak would be 8.8%, since there would be twice the probability that one of the two S atoms would be ^{34}S . With S_1 present in $m/z\ 64$, the residual 32 mass units must be assigned; O_2 is an obvious possibility. Each of these would contribute 0.2% to the probability of an isotopic $m/z\ 66$ peak, or with S_1 a total of 4.8%, agreeing well with the observed 5.0%. The mass-32 difference between M^+ and ^{32}S might also be assigned to CH_4O , but (as will be discussed in Section 2.3) this would cause a 1.1% ^{13}C contribution to $m/z\ 65$, which would make the predicted abundance much too large. [Sulfur dioxide]

Chemistry 212, Dr. Glaser

Exercise Assignment: Applications of Mass Spectroscopy

In Unknown 2.4, calculate (after checking for (M+2) elements) the maximum number of carbon atoms in the ions m/z 43 and 58. The results indicate that m/z 43 is formed from m/z 58 by the loss of what group?

Unknown 2.4

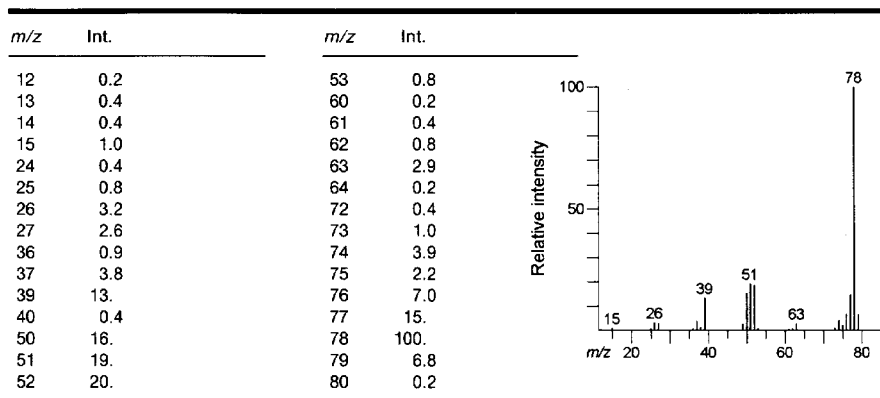


2.4. If the mass-43 peak were due to $C_2H_3O^+$, the expected 44/43 intensity ratio would be 2.2% from the two ^{13}C atoms present. Thus the observed ratio corresponds more closely to that predicted for three carbon atoms, such as in the ion formula $C_3H_7^+$. However, one should always be aware of the possible contribution from "background" in the instrument, which is much more likely to give a high (*not* low; why?) indication of the number of carbon atoms. On the other hand, if an oxygen atom is present in the m/z -43 ion, there should be a 0.2% contribution to the m/z 45 peak due to $C_2H_3^{18}O$; unfortunately, this is just on the limit of the absolute error assumed possible in the intensity data of these unknown spectra.

To calculate the number of carbon atoms in the large m/z 58 peak, note that the intensity ratio of masses 59/58 is 4.4%. From this, Table 2.2 indicates four carbon atoms; a smaller number would not be possible unless m/z 59 contained an impurity or extraneous fragment-ion contribution. Thus m/z 58 corresponds to C_4H_{10} (butane). The loss of 15 to give the base peak at m/z 43 is most logically a methyl group, confirming the prediction of the formula $C_3H_7^+$ for this fragment ion. [Butane]

The Unknown 2.5 has a small but important peak at m/z 80. The m/z 79 peak could not be consistently explained if the m/z 80 would be taken as indicative of ^{18}O . Why not. What is this compound?

Unknown 2.5

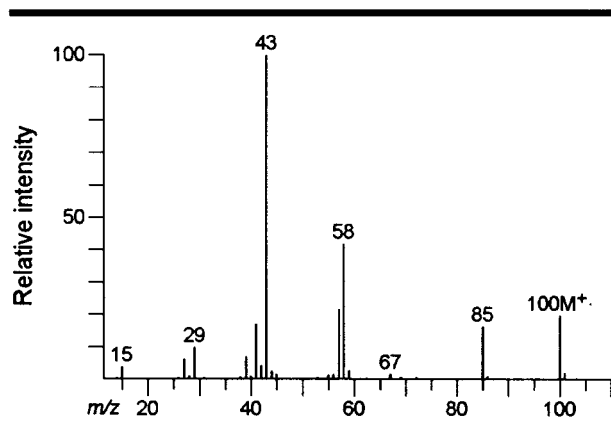


2.5. The $[m/z\ 79]/[m/z\ 78]$ value of 6.8% corresponds nicely to six carbon atoms (Table 2.2). By difference there should also be six hydrogen atoms in m/z 78, for a probable elemental composition of C_6H_6 . The aromatic molecule benzene is a possible structure whose molecular ion should have the indicated high stability. [Benzene]

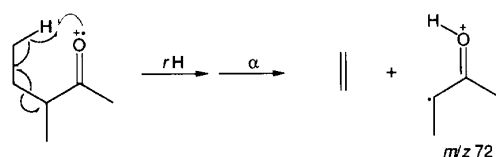
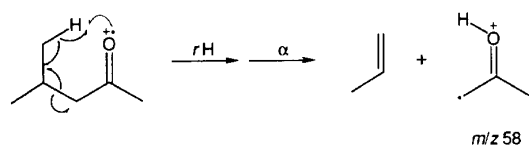
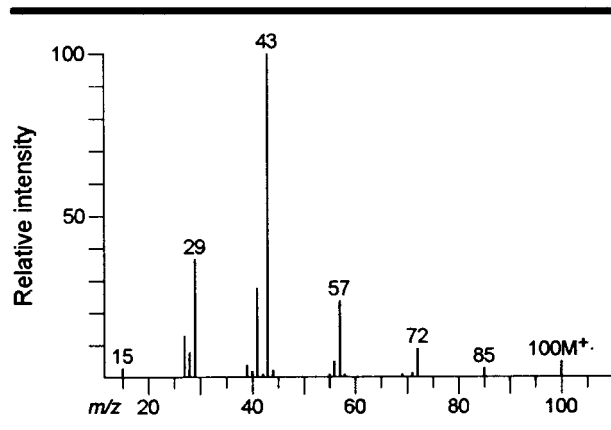
McLafferty Rearrangement of Ketones

These are the spectra of 3- and 4-methyl-2-pentanone. Which one is which?

Unknown 4.16



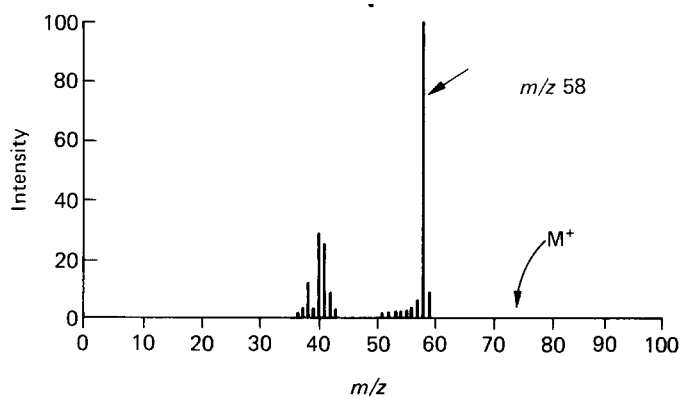
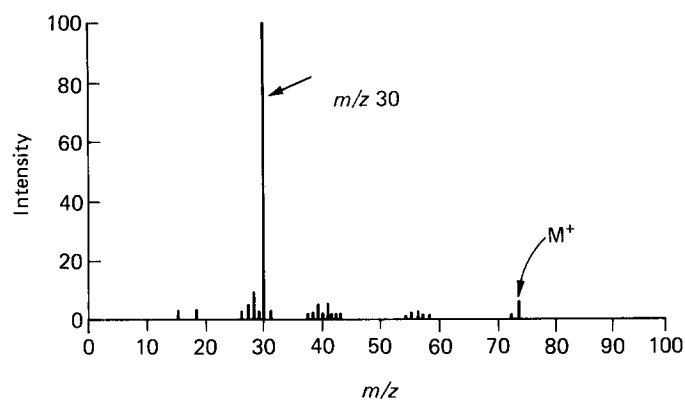
Unknown 4.17



Mass Spectra of Isomeric Amines

These are the spectra of isobutylamine and of t-butylamine. Which one is which?

Discuss the fragmentation paths for the isomers.



Top Spectrum: Isobutylamine, $\text{Me}_2\text{CHCH}_2\text{NH}_2$.

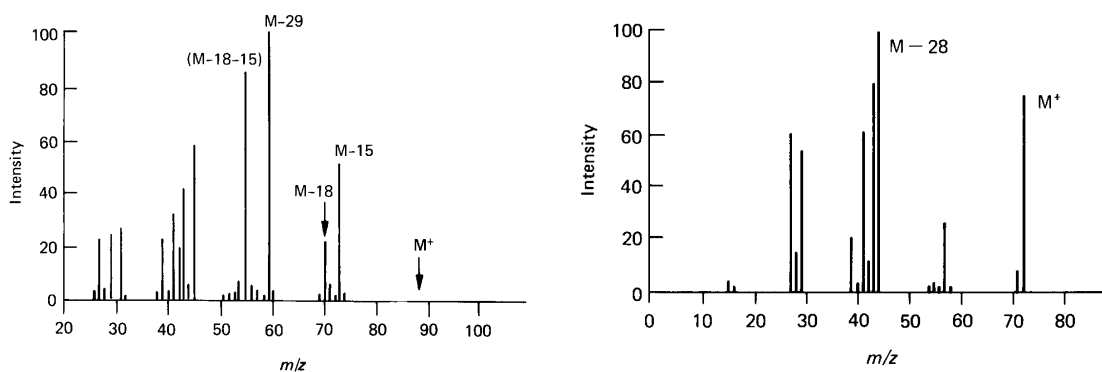
The $m/z=30$ peak corresponds to the $\text{H}_2\text{C}=\text{NH}_2$ cation and comes from homolytic beta-C-C fragmentation of the molecular ion.

Bottom Spectrum: Tert. Butylamine, Me_3CNH_2 .

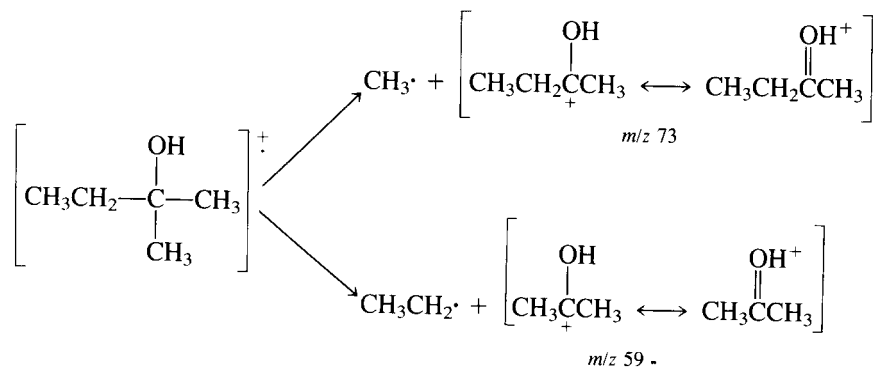
The $m/z=58$ peak is $\text{Me}_2\text{C}=\text{NH}_2$ cation and comes from homolytic beta-C-C fragmentation of the molecular ion.

Mass Spectra of Oxygen Containing Compounds

These are the spectra of an alcohol and of an aldehyde. Which one is which? Give the structures of the compounds and explain the fragmentation patterns observed.



Top Spectrum: 2-methyl-2-butanol, $\text{H}_3\text{C}-\text{CH}_2-\text{CMe}_2-\text{OH}$.



Bottom Spectrum: Butyraldehyde = Butanal.

Main peak due to McLafferty rearrangement! Peak at 44 is due to the enol cation and it is 28 below molecular mass and indicates elimination of ethene.