Interpretation of Mass Spectral Data

1) The molecular ion

The molecular ion in an E.I. spectrum may be identified using the following rules:

1) It must be the ion of highest m/z in the spectrum, apart from isotope peaks resulting from its molecular formula. Conventionally in mass spectrometry, we calculate the molecular weight using the masses of the most abundant isotopes of all the elements in the compound. e.g. for chlorothiophene we calculate the molecular weight as ${}^{12}C_4{}^{1}H_3{}^{32}S_1{}^{35}Cl_1$ = 118 Da
The possibility of higher m/z peaks due to impurities should also be considered.

2) In an E.I. spectrum, the molecular ion is formed by loss of an electron; therefore 1 electron is unpaired, making it a radical species. Such ions are known as "odd-electron" (OE) ions.

If the molecular formula of an ion is known (or suspected), the "rings and double bonds" formula may be used to determine whether it is an even- or odd-electron species. This formula may be generalised as:
For a formula $C_x H_y N_z O_n$, The number of rings plus double bonds is given by $x - y/2 + z/2 + 1$. This calculation will yield a whole number for an odd-electron ion, and a number ending in 1/2 for an even-electron ion. Other atoms in the formula are counted as equivalent to whichever of C, H, N or O they correspond to in valence. e.g. Si is equivalent to C, halogens are equivalent to H, P is equivalent to N.

3) The ion must obey the "nitrogen rule". This states that, for compounds containing most of the elements common in organic chemistry, for a molecule to have an odd numbered molecular weight, it must contain an odd number of nitrogen atoms. If a molecule contains an even number of nitrogen atoms, or no nitrogen atoms at all, then it will have an even-numbered molecular weight. This fact arises from the fact that nitrogen has an even mass and an odd valency.

4) The assumed molecular ion must be capable of producing the high mass fragments in the spectrum by plausible losses of neutral fragments.

2) Isotopes

Many elements have more than 1 stable isotope. The effect of naturally-occurring isotopes is to produce peaks in the mass spectrum other than the "main" peak (the peak due to the most abundant isotopes). In the spectrum of chlorothiophene, the peaks at m/z 118 and 120 represent the contributions from the two isotopes of chlorine, ${}^{35}Cl$ and ${}^{37}Cl$.
Elements which have isotopes at "A+2" values are chlorine, bromine, oxygen (very weak, only 0.2%), silicon and sulphur. Of these, chlorine and bromine are readily recognisable.
Elements which have isotopes at "A+1" values are carbon and nitrogen.

3) Accurate mass measurements

Using the appropriate instrument and techniques, the masses of ions may be determined with accuracies of the order of <10 ppm. This information can be used to determine the elemental composition of any ion, due to the fact that the exact masses of the isotopes of element are, with the exception of the carbon 12 standard, not whole numbers. e.g. the "nominal" mass of acetone (C_3H_6O) is 3x12 + 6x1 + 1x16 = 58. The exact mass of this elemental combination is, taking the mass of ${}^{12}C$ as 12.000000, ${}^{1}H$ as 1.0078246 and ${}^{16}O$ as 15.994915, 58.04186. Using accurate mass measurement, this can be readily distinguished from the mass of butane (C_4H_{10}) which is 58.07825.

4) The general appearance of the spectrum

The intensity of the molecular ion usually parallels the chemical stability of the molecule, and compounds with high unsaturation (numbers of rings and double bonds) show the most abundant molecular ions.
For aromatic compounds containing an alkyl chain, the abundance of the molecular ion will decrease with increasing length of the alkyl chain.