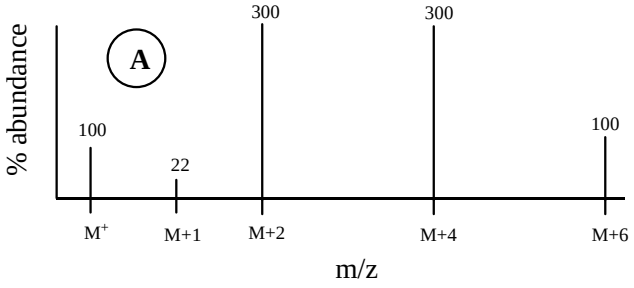
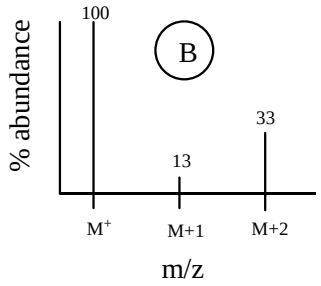
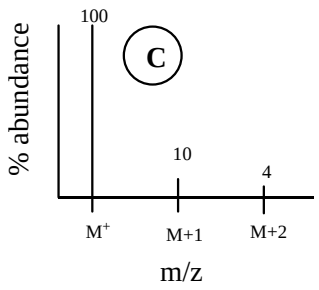
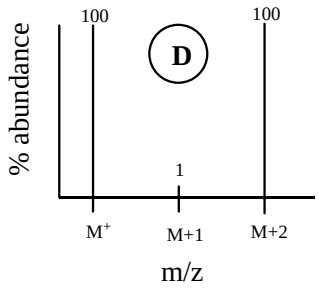
T8 Practice problems (Refer to pages C95-C98 in the online manual)

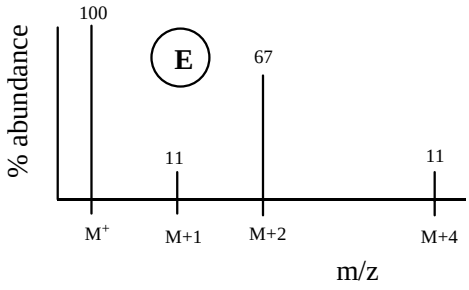
1. Use the pattern of the parent ion and isotope peaks seen in the mass spectrum to predict the correct formula of molecules A-G.

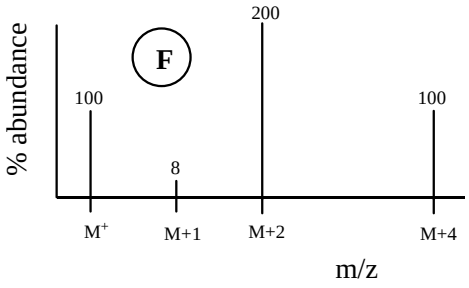


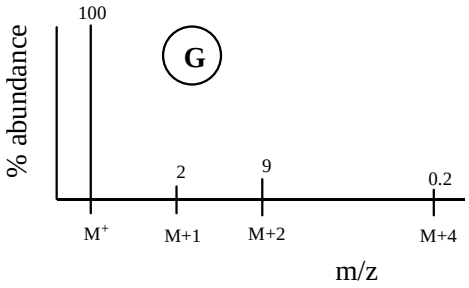












Mass Spectrum	#C	#S	#Cl	#Br
A	20	-	-	3
B	12	-	1	-
C	9	1	-	-
D	1	-	-	1
E	10	-	2	-
F	7	-	-	2
G	2	2	-	-

2. Compound information: M^+ = 59.031 +/- 0.025 g/mol

C	H	N	O	m/z
1	1	1	2	59.000727
1	5	3	-	59.048345
2	5	1	1	59.037111
3	9	1	-	59.073496

Options of $C_1H_5N_3$ and C_2H_5NO are both possible.

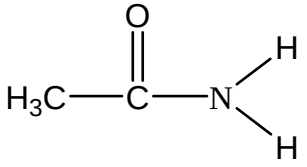
IR shows peaks at 3380(s, two bands) and 1675 (s) cm^{-1}
1675 cm^{-1} is a carbonyl so the molecule contains Oxygen and the formula must be C_2H_5NO.

Major MS fragments and features:

m/e	% abundance	interpretation
59	***100***	***parent ion, M^+***
44	***77***	***loss of CH_3 from M^+, leaving $CONH_2^+$***
43	***58***	***loss of O or NH_2 from M^+, leaving CH_3CO^+ or $CH_3CNH_2^+$***
42	***28***	***loss of O and H from M^+, leaving CH_3CNH^+***

Structure and conclusions:

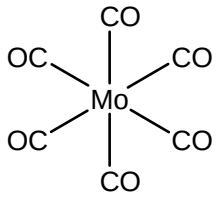
acetamide



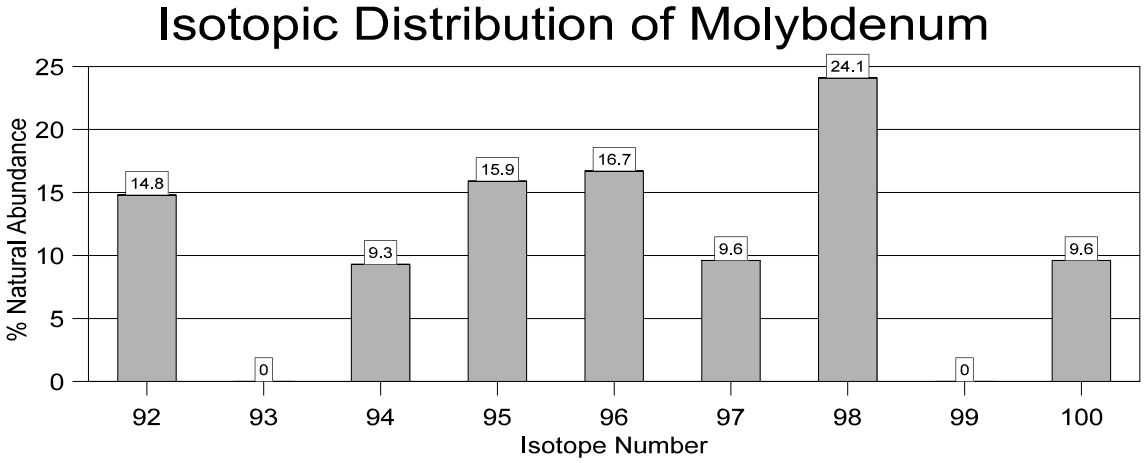
confirmed by:

- ***IR shows presence of 1º amine (NH_2) at ~3400 cm^{-1} and a carbonyl on an amide group ($O=C-NH_2$) at ~1690 cm^{-1}.***

3. Compound information:



a) Draw a stick-plot of the % natural abundance vs isotope number for molybdenum. (*Hint: isotopic abundances are available in the CRC or on-line at* http://www.webelements.com)



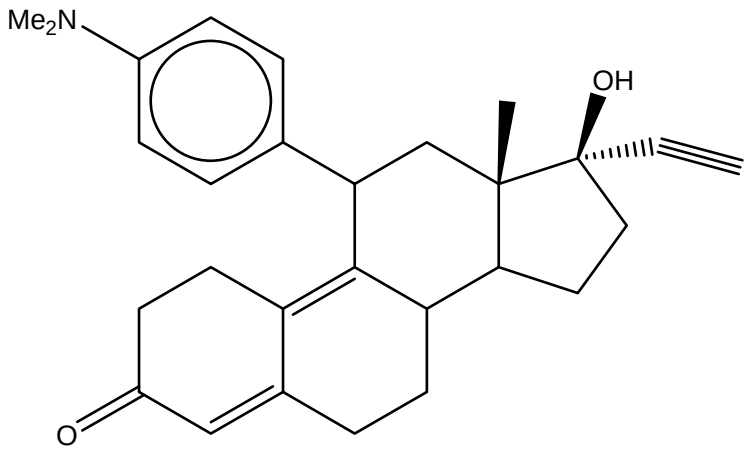
b) Analyze the mass spectrum (previous page)and complete the table to assign all significant fragments of the $Mo(CO)_6$ sample. In the second m/e column, assign one fragment (of your choice) in enough detail to show all isotopes of the metal center.

m/e	% relative abundance	fragment	m/e	% relative abundance	fragment
266	66	$^{98}Mo(CO)_6^+$	***100***	***22***	$^{100}\mathbf{Mo}^+$
238	***8***	$^{98}\mathbf{Mo(CO)_5}^+$	***98***	***54***	$^{98}\mathbf{Mo}^+$
210	***12***	$^{98}\mathbf{Mo(CO)_4}^+$	***97***	***21***	$^{97}\mathbf{Mo}^+$
182	***100***	$^{98}\mathbf{Mo(CO)_3}^+$	***96***	***36***	$^{96}\mathbf{Mo}^+$
154	***56***	$^{98}\mathbf{Mo(CO)_2}^+$	***95***	***35***	$^{95}\mathbf{Mo}^+$
126	***43***	$^{98}\mathbf{Mo(CO)_1}^+$	***94***	***19***	$^{94}\mathbf{Mo}^+$
			92	***35***	$^{92}\mathbf{Mo}^+$

c) How do the patterns seen in the mass spectrum of $Mo(CO)_6$ compare to the stick-plot drawn in question (a)?

Same overall pattern seen in each fragment containing Mo as seen in the stick-plot.

4.



Examine the structure at left to answer the following questions.

a) Where would you find $\pi_3 \rightarrow \pi_3^*$ for the diene-one chromophore?

$\pi \rightarrow \pi^*$ base value of 190 for the C=O + 2(30) for two conjugated double bonds = 250 nm

b) What ε value would this absorption have?

$\pi \rightarrow \pi^*$ is an allowed transition, so $\varepsilon > 1000$

c) Where would you find $n \rightarrow \pi_3^*$ for diene-one chromophore?

$n \rightarrow \pi_3^*$ base value of 280 for the C=O + 2(30) for two conjugated double bonds = 340 nm

d) What ε value would this absorption have?

$n \rightarrow \pi_3^*$ is an forbidden transition, so $\varepsilon < 50$

e) Where would you expect to find the longest wavelength absorption for the most intense transition of the amino-benzene chromophore?

longest wavelength means the most conjugated version of the transition, most intense means largest ε value so together this question is asking about the conjugated $\pi \rightarrow \pi^*$
$\pi \rightarrow \pi^*$ base value of 190 for the amine + 3(30) for three conjugated double bonds = 280 nm

f) Where would you expect to find $\pi \rightarrow \pi^*$ for the acetylene chromophore?

$\pi \rightarrow \pi^*$ base value of 190 nm