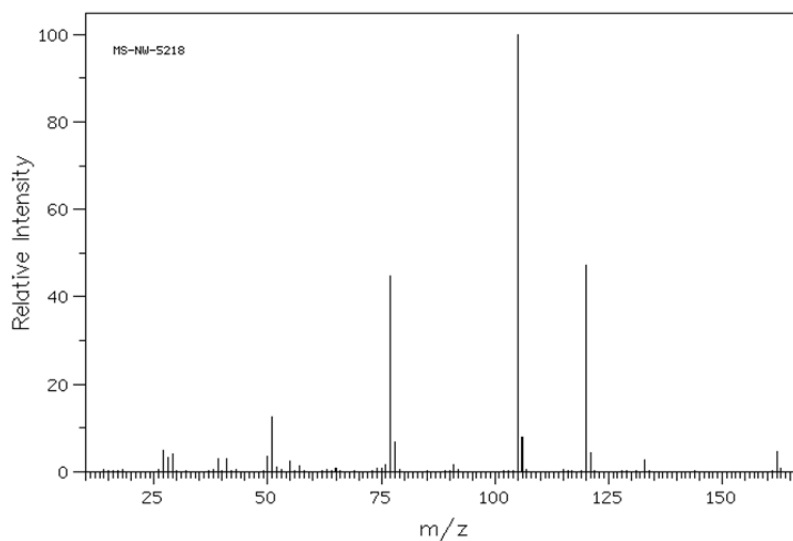


Mass Spec and Molecular Formula
S343 Problem Set

Basic questions:

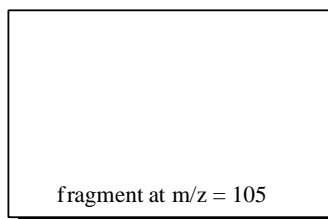
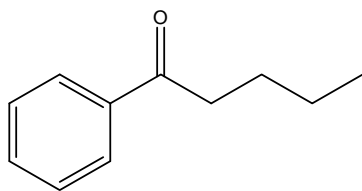
Read Technique 23 in Techniques in Organic Chemistry and do problems 2, 3, 4, 8

1. Give three molecular formulas that are consistent with $M^+ = 122$.
2. Why is there a small peak at $M^+ = 32$ for CH_3NH_2 ?
3. What is a MS library, and how is it used?
4. What is high resolution MS, and what advantage does it have over low resolution MS?
5. The questions below refer to this Mass Spectrum of 1-phenylpentan-1-one:

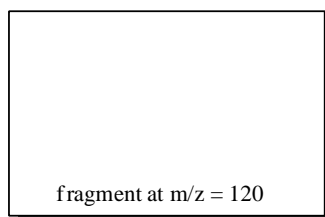
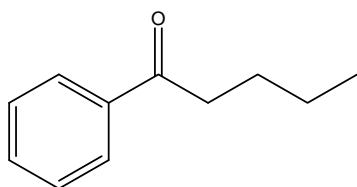


A. What causes the small peak at m/z 162?

B. Provide a mechanism and fragment structure that lead to formation of the base peak at $m/z = 105$.

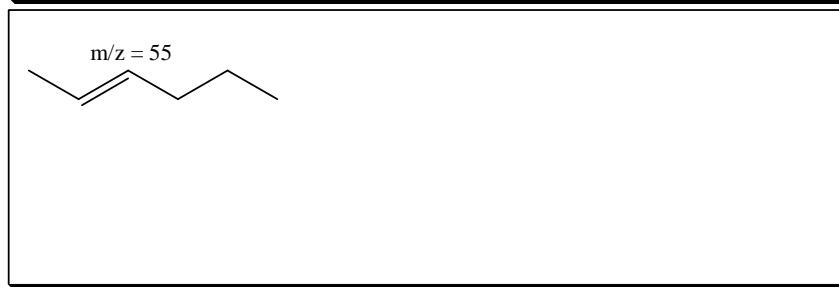
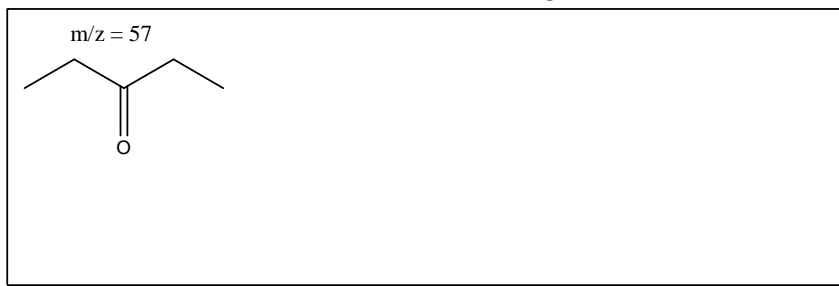


C. Provide a mechanism and fragment structure that lead to formation of the significant peak at $m/z = 120$.

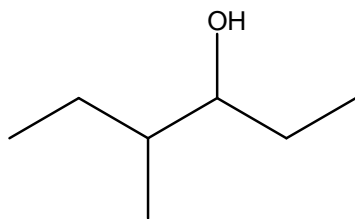


6. Use the rule of 13 to come up with 3 likely formulas that fit $M^+ = 102$.

7. Provide mechanisms to account for the fragments seen in the mass spectrum of these compounds.



8. Give the m/z values of two major fragments you would expect to see in the mass spectrum of the following compound. Mark the one that is most likely to show up as the base peak, and explain.



$m/z =$

$m/z =$

9. What two circumstances lead to fragments with even m/z values?

10. Give three important pieces of information about the molecular formula of the compound (other than the molecular weight) that you can obtain from this mass spec data.

m/z	Relative abundance
34	21
52	35
91	100
102	22
111 (M^+)	10
113	3.3

11. What are these abbreviations: CI, EI, FAB, ESI, MALDI-TOF

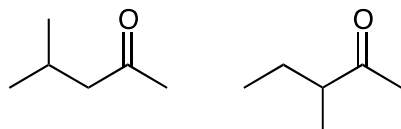
Problems

MS Problem Solving Guide

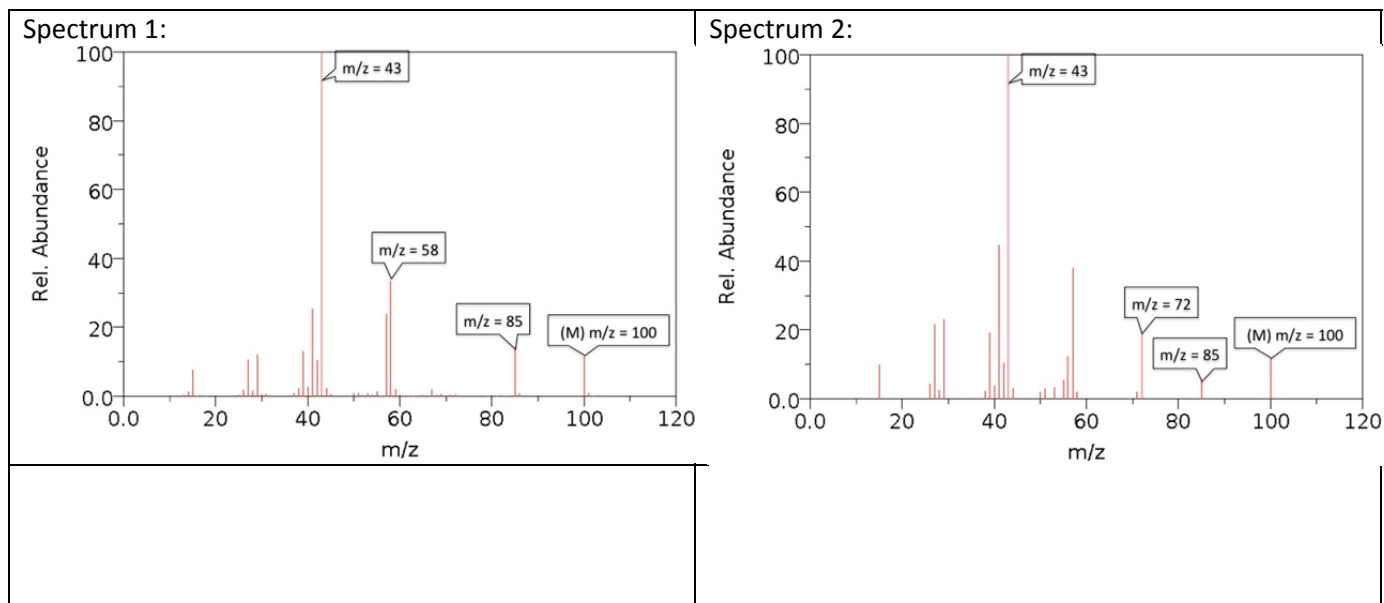
1. Identify molecular ion (M). Note its abundance (sometimes it's not there at all).
 2. Look at isotope pattern: M+1 peak can tell you # of carbons, and compounds containing Br, Cl, S, Si can be identified from M+2 peak.
 3. Apply rule of 13 to get molecular formula (CH).
 4. Apply nitrogen rule. (Odd M often corresponds to odd # N in molecule).
 5. Calculate UN, and predict molecular formula. (Might have to include heteroatoms)
 6. Draw possible structures, and predict major fragmentations.
 7. Analyze spectrum and deduce most likely structure(s).
1. The mass spectrum of an unknown compound shows the following peaks. Determine the molecular formula and propose a structure.

<i>m/z</i>	Relative Abundance
43	100 (base)
78	23.6 (M)
79	1.00
80	7.55
81	0.25

2. The EI mass spectra of the following ketones are shown below.



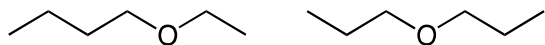
a) Determine which mass spectrum corresponds to each compound, and label the spectra underneath in the space provided.



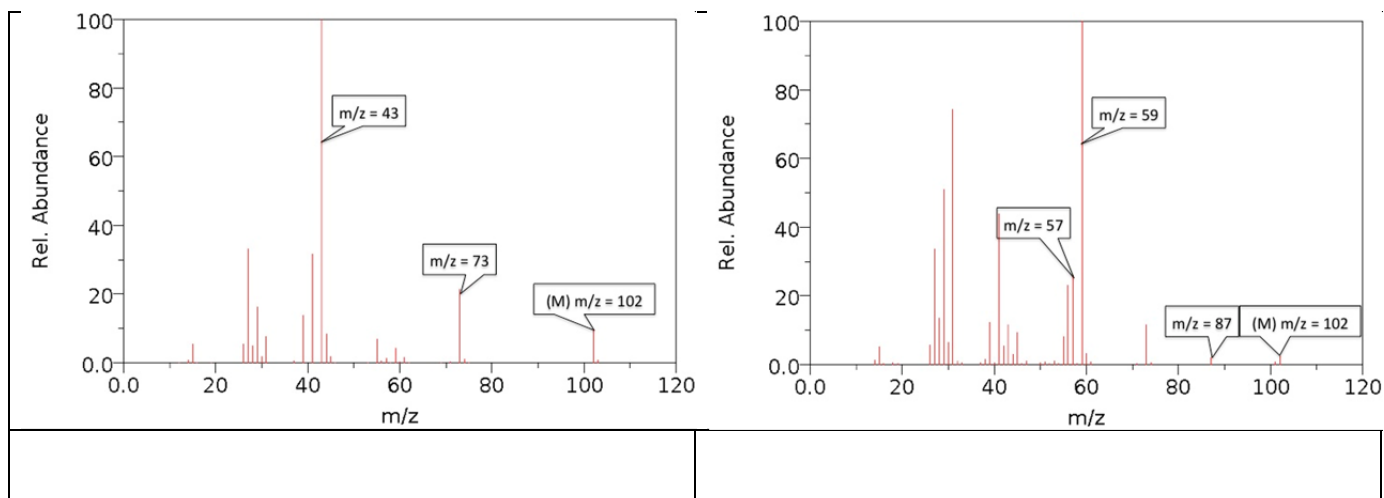
b) Provide structures for each labeled ion in the space provided below. All charges, number of hydrogens, and number of electrons must be clearly indicated.

Spectrum 1	Structure of ion	Spectrum 2	Structure of ion
m/z = 100		m/z = 100	
m/z = 85		m/z = 85	
m/z = 58		m/z = 72	
m/z = 57		m/z = 57	
m/z = 43		m/z = 43	

3. The EI mass spectra of the following two ethers are shown below.



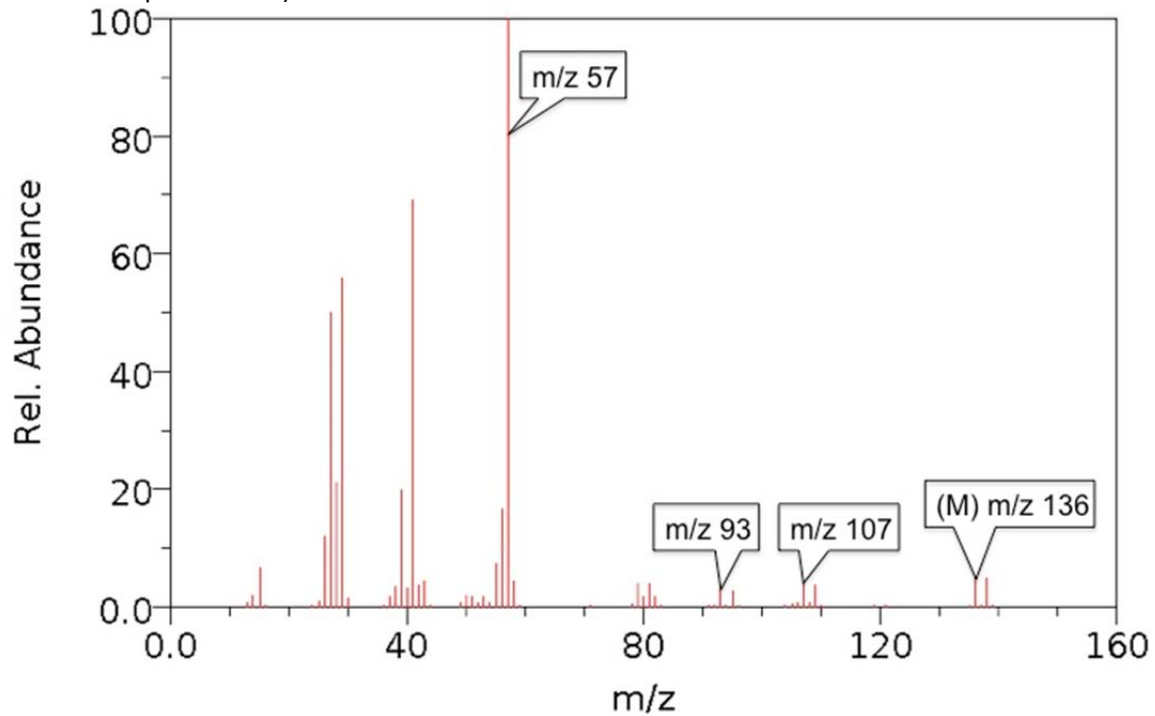
a) Determine which mass spectrum corresponds to each compound, and label the spectra underneath in the space provided.



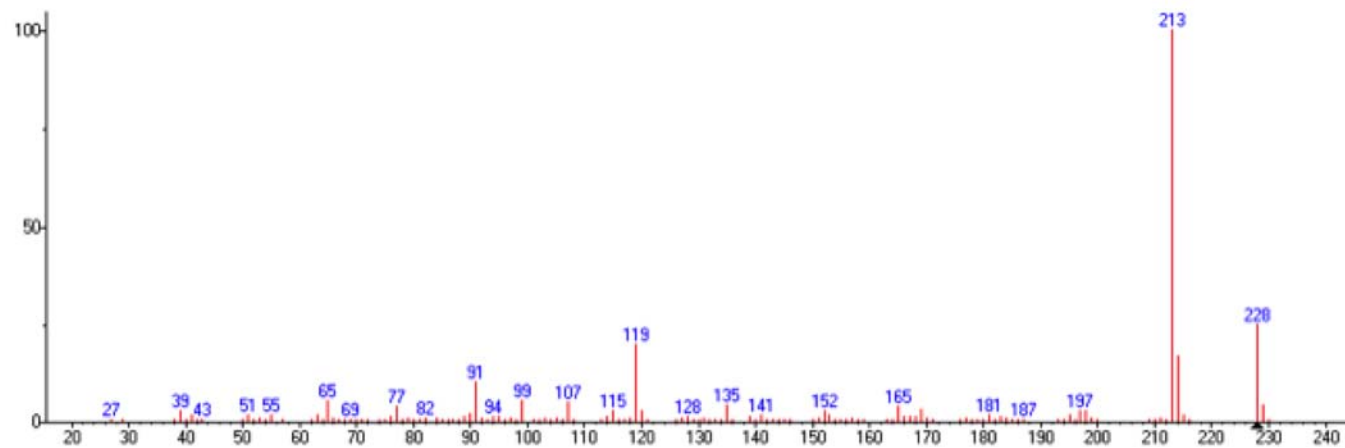
b) Provide structures for each labeled ion in the space provided below. All charges, number of hydrogens, and number of electrons must be clearly indicated.

Spectrum 1	Structure of ion	Spectrum 2	Structure of ion
m/z = 102		m/z = 102	
m/z = 73		m/z = 87	
m/z = 43		m/z = 59	
		m/z = 57	

4. Determine the structure of the unknown and account for fragments at 136, 107, 93, and 57. (Why is there no M+2 peak at 59?)

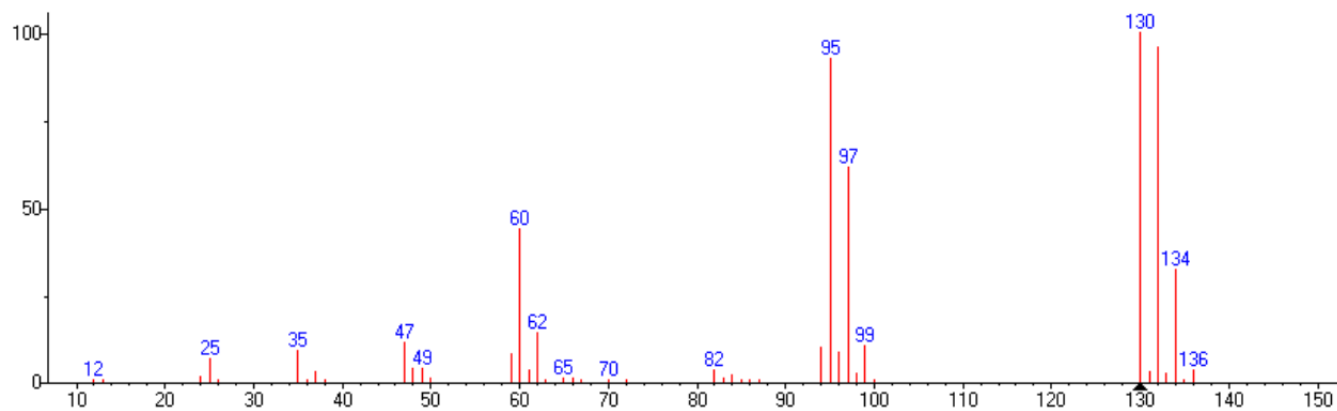


5. How many C atoms does the following molecule most likely contain? (M = 228)



m/z	int	m/z	int	m/z	int	m/z	int	m/z	int	m/z	int
27	5	78	7	104	5	135	43	168	13	211	9
39	29	79	11	105	11	136	4	169	30	213	999
41	16	82	10	107	51	139	12	170	9	214	169
50	5	84	8	114	12	141	15	171	5	215	17
51	15	89	14	115	29	142	5	176	6	228	248
53	10	90	21	116	5	144	6	177	11	229	41
55	15	91	100	118	8	145	7	181	16	230	4
62	5	92	10	119	198	151	9	182	5		
63	18	94	12	120	28	152	26	183	14		
64	7	95	13	121	5	153	15	184	9		
65	53	97	9	127	11	155	6	194	6		
66	10	99	52	128	14	157	11	195	17		
75	7	101	7	131	10	165	38	197	29		
76	14	102	5	133	5	166	14	198	26		
77	38	103	8	134	6	167	12	199	10		

6. How many C and Cl atoms does the following molecule most likely contain? (M = 130)



m/z	int	m/z	int	m/z	int	m/z	int
24	17	60	438	94	100	134	322
25	65	61	36	95	924	135	7
35	90	62	141	96	85	136	35
36	8	65	13	97	613		
37	30	66	12	98	24		
47	112	70	5	99	102		
48	39	82	34	130	999		
49	39	83	11	131	25		
50	13	84	22	132	954		
59	83	85	7	133	24		

7. The mass spectrum of an unknown molecule shows a molecular ion peak at $m/z = 73$. Provide a reasonable structure.

8. A researcher analyzed an unknown solid (MW = 420) to determine its percent composition. An 11.32 mg sample was burned in a combustion apparatus. The carbon dioxide (24.87 mg) and water (5.82 mg) were collected and weighed. **Determine the empirical and molecular formulas of the unknown, and the Unsaturation Number (UN).**

Atom	Atomic weight
C	12.011 g/mol
H	1.008 g/mol
O	16.000 g/mol

Empirical formula: _____

Molecular formula: _____

Unsaturation Number (UN): _____