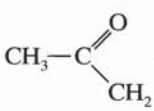
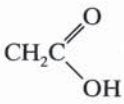
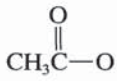
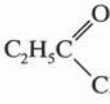
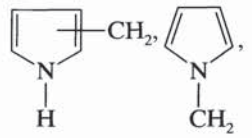
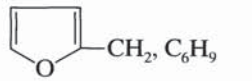
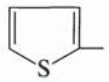
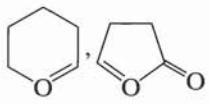
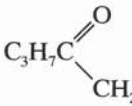
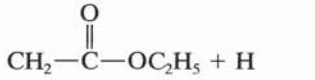
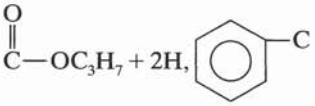
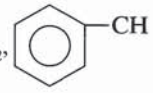
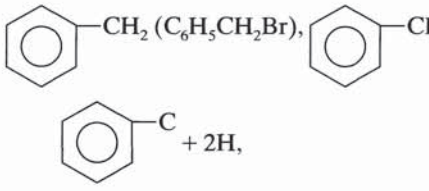
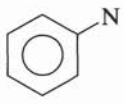
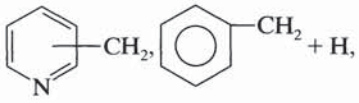
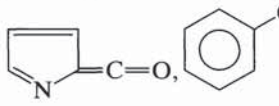
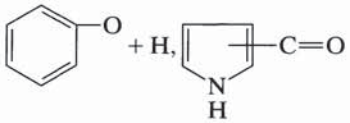
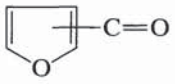
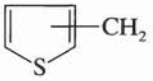
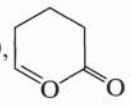
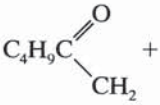
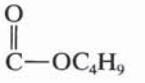
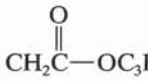
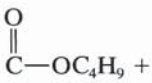
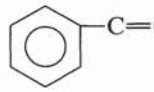
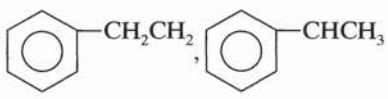
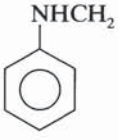
Appendix B Common Fragment Ions

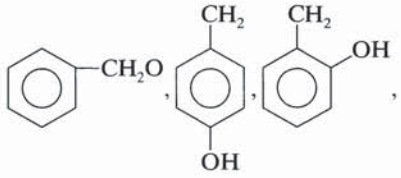
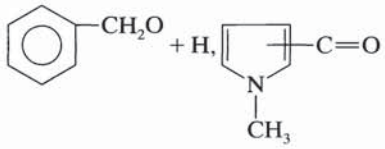
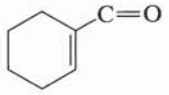
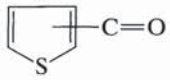
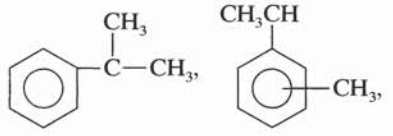
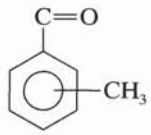
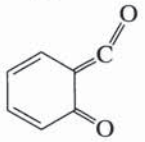
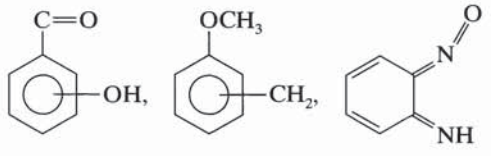
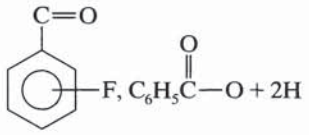
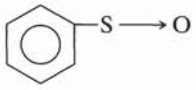
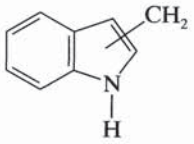
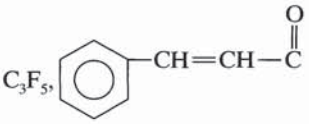
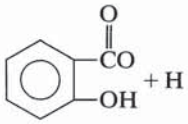
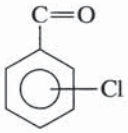
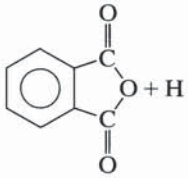
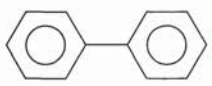
All fragments listed bear +1 charges. To be used in conjunction with Appendix C. Not all members of homologous and isomeric series are given. The list is meant to be suggestive rather than exhaustive. Appendix II of Hamming and Foster (1972), Table A-7 of McLafferty's (1993) interpretative book, and the high-resolution ion data of McLafferty (1982) are recommended as supplements. Structural inferences are listed in parentheses.

m/z Ions[a]	(Structural Inference)
14	CH_2
15	CH_3
16	O
17	OH
18	H_2O, NH_4
19	F, H_3O
26	$C{\equiv}N$, C_2H_2
27	C_2H_3
28	C_2H_4, CO, N_2 (air), $CH{=}NH$
29	C_2H_5, CHO
30	CH_2NH_2 (RCH_2NH_2), NO
31	CH_2OH (RCH_2OH), OCH_3
32	O_2 (air)
33	SH, CH_2F
34	H_2S
35	Cl (^{37}Cl at 37)
36	HCl (H ^{37}Cl at 38)
39	C_3H_3
40	$CH_2C{=}N$, Ar(air)
41	C_3H_5, $CH_2C{=}N$ + H,[a] C_2H_2NH
42	C_3H_6, C_2H_2O
43	C_3H_7, $CH_3C{=}O$, $CH_3C{=}OG$, (G = R, Ar, NH_2, OR, OH), C_2H_5N
44	$CH_2\overset{\overset{H}{\|}}{C}{=}O$ + H (Aldehydes, McLafferty rearrangement), CH_3CHNH_2, CO_2, $NH_2C{=}O$ ($RC{=}ONH_2$), $(CH_3)_2N$
45	$\overset{\overset{CH_3}{\|}}{C}HOH$, CH_2CH_2OH, CH_2OCH_3 (RCH_2OCH_3), $\overset{\overset{O}{\|}}{C}{-}OH$, $CH_3CH{-}O$ + H (CH_3CHOHR)
46	NO_2
47	CH_2SH (RCH_2SH), CH_3S
48	CH_3S + H
49	CH_2Cl (CH_2 ^{37}Cl at 51)
51	CHF_2, C_4H_3
53	C_4H_5
54	$CH_2CH_2C{\equiv}N$
55	C_4H_7, $CH_2{=}CHC{=}O$
56	C_4H_8
57	C_4H_9, $C_2H_5C{=}O$
58	 + H, $C_2H_5CHNH_2$, $(CH_3)_2NCH_2$, $C_2H_5NHCH_2$, C_2H_2S
59	$(CH_3)_2COH$, $CH_2OC_2H_5$,  , $NH_2\overset{\overset{CH_2}{\|}}{C}{=}O$ + H, CH_3OCHCH_3, CH_3CHCH_2OH, C_2H_5CHOH
60	 + H, CH_2ONO
61	 + 2H, CH_2CH_2SH, CH_2SCH_3
65	C_5H_5
66	 ≡ C_5H_6, H_2S_2 (RSSR)
67	C_5H_7
68	$CH_2CH_2CH_2C{\equiv}N$
69	C_5H_9, CF_3, $CH_3CH{=}CHC{=}O$, $CH_2{=}C(CH_3)C{=}O$
70	C_5H_{10}
71	C_5H_{11}, $C_3H_7C{=}O$
72	 + H, $C_3H_7CHNH_2$, $(CH_3)_2N{=}C{=}O$, $C_2H_5NHCHCH_3$ and isomers
73	Homologs of 59, $(CH_3)_3Si$
74	$CH_2{-}\overset{\overset{O}{\|}}{C}{-}OCH_3$ + H
75	$\overset{\overset{O}{\|}}{C}{-}OC_2H_5$ + 2H, $C_2H_5\overset{\overset{O}{\|}}{C}O$ + 2H, $CH_2SC_2H_5$, $(CH_3)_2CSH$, $(CH_3O)_2CH$, $(CH_3)_2SiOH$
76	C_6H_4 (C_6H_5X, C_6H_4XY)
77	C_6H_5 (C_6H_5X)
78	C_6H_5 + H
79	C_6H_5 + 2H, Br (^{81}Br at 81)

Appendix B Continued

***m/z* Ions**[a]	**(Structural Inference)**
80	 CH_3SS + H, HBr ($H^{81}Br$ at 82)
81	 C_6H_9
82	$CH_2CH_2CH_2CH_2C{\equiv}N$, CCl_2 ($C^{35}Cl^{37}Cl$ at 84, $C^{37}Cl_2$ at 86), C_6H_{10}
83	C_6H_{11}, $CHCl_2$ ($CH^{35}Cl^{37}Cl$ at 85, $CH^{37}Cl_2$ at 87), 
85	C_6H_{13}, $C_4H_9C{=}O$, $CClF_2$ ($C^{37}ClF_2$ at 87), 
86	 + H, $C_4H_9CHNH_2$ and isomers
87	 homologs of 73, $CH_2CH_2COCH_3$
88	
89	
90	CH_3CHONO_2, 
91	 $(CH_2)_4Cl$ [$(CH_2)_4{}^{37}Cl$, at 93], 
92	 + H,
93	CH_2Br ($CH_2{}^{81}Br$ at 95, RCH_2Br), C_7H_9,  , C_7H_9 (terpenes)
94	
95	
96	$CH_2CH_2CH_2CH_2CH_2C{\equiv}N$
97	C_7H_{13}, 
98	
99	C_7H_{15}, $C_6H_{11}O$, 
100	 + H, $C_5H_{11}CHNH_2$
101	
102	
103	 + 2H, $C_5H_{11}S$, $CH(OCH_2CH_3)_2$
104	$C_2H_5CHONO_2$
105	 , $C_6H_5(C{=}O)G$[G = OH, OR, OAr, halogen, NH_2], 
106	

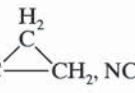
Appendix B *Continued*

m/z Ions[a]	(Structural Inference)
107	
	C_2H_4Br ($C_2H_4{}^{81}Br$ at 109)
108	
109	
111	
119	CF_3CF_2,
	
	
120	
121	
	C_9H_{13} (terpenes)
122	
123	
125	
127	I
128	HI
130	
131	
135	$(CH_2)_4Br$ [$(CH_2)_4{}^{81}Br$ at 137]
138	
139	
141	CH_2I (RCH_2I)
147	$(CH_3)_2Si{=}O{-}Si(CH_3)_3$
149	
154	

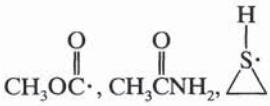
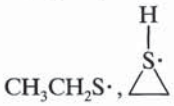
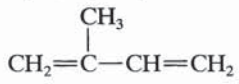
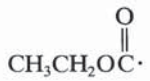
[a] Ions indicated as a fragment + nH (n = 1, 2, 3, . . .) are ions that arise via rearrangement involving hydrogen transfer.

Appendix C Common Fragments Lost

This list is suggestive rather than comprehensive. It should be used in conjunction with Appendix B. Table 5-19 of Hamming and Foster (1972) and Table A-5 of McLafferty (1993) are recommended as supplements. All of these fragments are lost as neutral species.

Molecular Ion Minus	Fragment Lost (Inference Structure)
1	H·
2	2H·
15	CH_3·
16	O ($ArNO_2$, amine oxides, sulfoxides); ·NH_2 (carboxamides, sulfonamides)
17	HO·
18	H_2O (alcohols, aldehydes, ketones)
19	F·
20	HF
26	CH≡CH, ·CH≡N
27	CH_2=CH·, HC≡N (aromatic nitrites, nitrogen heterocycles)
28	CH_2=CH_2, CO, (quinones) (HCN + H)
29	CH_3CH_2·, (ethyl ketones, $ArCH_2CH_2CH_3$), ·CHO
30	NH_2CH_2·, CH_2O ($ArOCH_3$), NO ($ArNO_2$), C_2H_6
31	·OCH_3(methyl esters), ·CH_2OH, CH_3NH_2
32	CH_3OH, S
33	HS· (thiols), (·CH_3 and H_2O)
34	H_2S (thiols)
35	Cl·
36	HCl, $2H_2O$
37	H_2Cl (or HCl + H)
38	C_3H_2, C_2N, F_2
39	C_3H_3, HC_2N
40	CH_3C≡CH
41	CH_2=$CHCH_2$·
42	CH_2=$CHCH_3$, CH_2=C=O,  , NCO, $NCNH_2$
43	C_3H_7·(propyl ketones, $ArCH_2$—C_3H_7), $CH_3\overset{\overset{O}{\|}}{C}$·(methyl ketones, $CH_3\overset{\overset{O}{\|}}{C}$G, where G = various functional groups), CH_2=CH—O·, (CH_3· and CH_2=CH_2), HCNO
44	CH_2=CHOH, CO_2 (esters, anhydrides), N_2O, $CONH_2$, $NHCH_2CH_3$
45	CH_3CHOH, CH_3CH_2O·(ethyl esters), CO_2H, $CH_3CH_2NH_2$
46	(H_2O and CH_2=CH_2), CH_3CH_2OH, ·NO_2 ($ArNO_2$)
47	CH_3S·
48	CH_3SH, SO (sulfoxides), O_3
49	·CH_2Cl
51	·CHF_2
52	C_4H_4, C_2N_2
53	C_4H_5
54	CH_2=CH—CH=CH_2
55	CH_2=$CHCHCH_3$

Appendix C Continued

Molecular Ion Minus	Fragment Lost (Inference Structure)
56	$CH_2{=}CHCH_2CH_3$, $CH_3CH{=}CHCH_3$, 2CO
57	$C_4H_9\cdot$ (butyl ketones), C_2H_5CO (ethyl ketones, EtC=OG, G = various structural units)
58	$\cdot NCS$, (NO + CO), CH_3COCH_3, C_4H_{10}
59	
60	C_3H_7OH, $CH_2{=}C(OH)_2$ (acetate esters)[a]
61	
62	(H_2S and $CH_2{=}CH_2$)
63	$\cdot CH_2CH_2Cl$
64	C_5H_4, S_2, SO_2
68	
69	$CF_3\cdot$, $C_5H_9\cdot$
71	$C_5H_{11}\cdot$
73	
74	C_4H_9OH
75	C_6H_3
76	C_6H_4, CS_2
77	C_6H_5, CS_2H
78	C_6H_6, CS_2H_2, C_5H_4N
79	$Br\cdot$, C_5H_5N
80	HBr
85	$\cdot CClF_2$
100	$CF_2{=}CF_2$
119	$CF_3{-}CF_2\cdot$
122	C_6H_5COOH
127	$I\cdot$
128	HI

[a] McLafferty rearrangement.