

ESPECTROMETRIA DE MASSAS

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Quais informações esta técnica me fornece?

- ▶ Determinar a massa molecular
- ▶ Fórmula molecular
- ▶ Características estruturais

No passado...

A massa molecular era determinada

- ▶ por densidade vapor
- ▶ Ponto de fusão

Fórmula molecular

- ▶ Análise elementar

Técnicas lentas e precisavam de grandes quantidades

HOJE???!!

- ▶ CG-EM
- ▶ HPLC-MS
- ▶ Fontes de ionização :
- ▶ ionização por elétrons (*electron ionization* - EI)
(amostras gasosas)
- ▶ ionização por eletrospray (*electrospray ionization* - ESI) (líquidas)
- ▶ fontes de ionização

dessorção/ionização a laser assistida por matriz – *matrix assisted laser desorption/ionization* - MALDI (sólidos)

- ▶ MALDI-TOFF

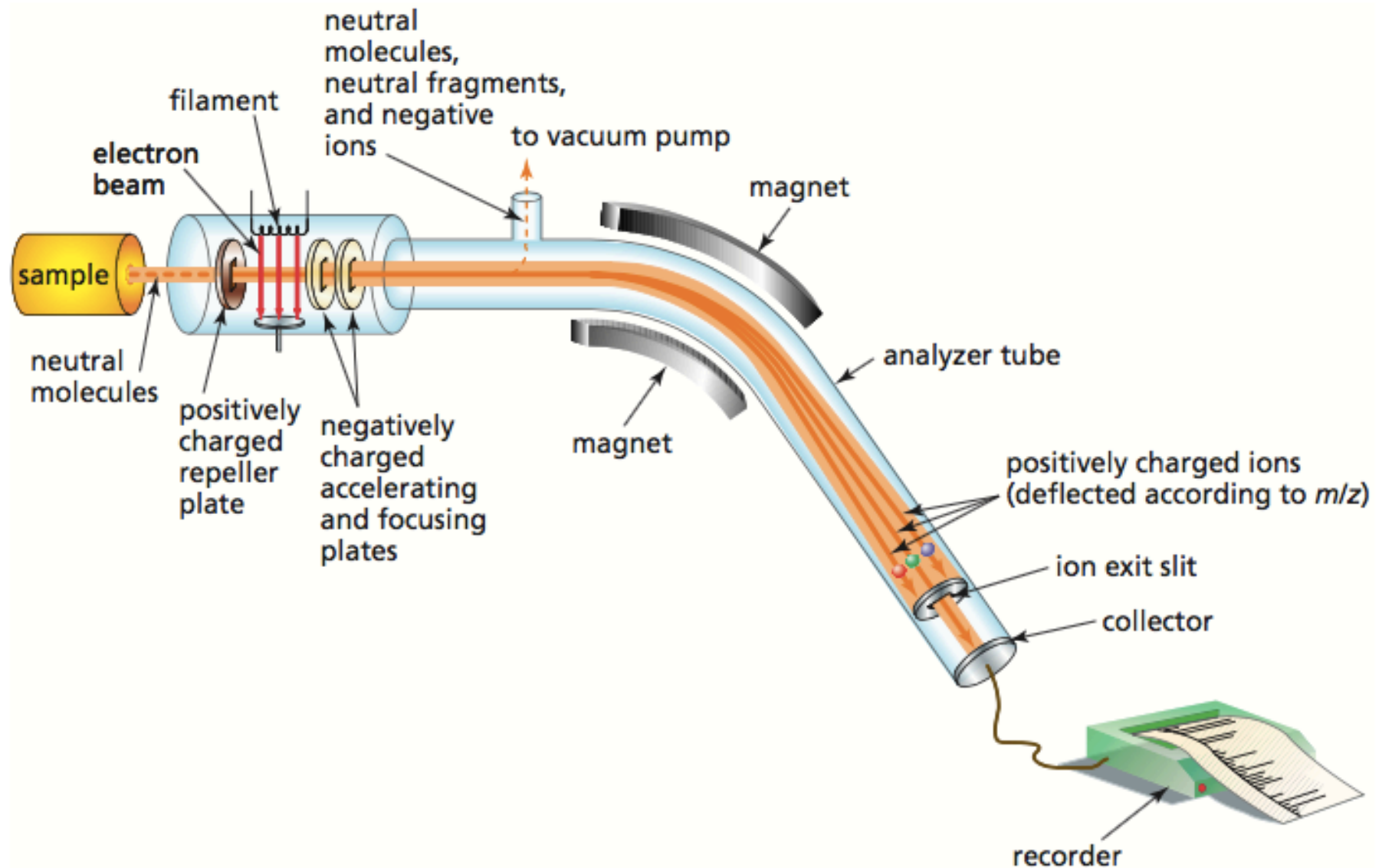
Técnica de EI

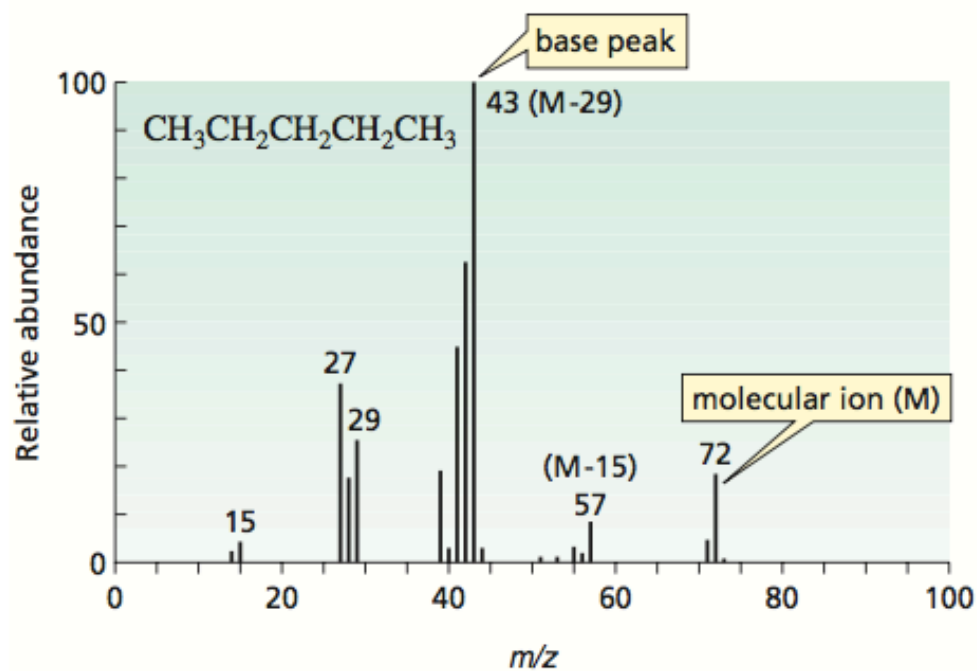
- ▶ moléculas voláteis e termooestáveis
- ▶ a alta energia proveniente dos elétrons (70 eV) pode causar excessiva dissociação iônica
- ▶ íon molecular pode não ser observado
- ▶ Dificultando processo de elucidação estrutural

Técnica de ionização química (*chemical ionization* – CI)

- ▶ gás reagente na câmara de ionização
- ▶ as moléculas de metano, geram espécies protonadas e transferem seus prótons o analito.
- ▶ técnica de ionização
- ▶ Facilita para ver o íon molecular da amostra

Espectrometria de Massa





m/z	Relative abundance
73	0.52
72	18.56
71	4.32
57	11.20
43	100.00
42	55.27
41	37.93
39	12.44
29	26.65
28	17.75
27	31.22
15	4.22
14	2.56

◀ Figure 13.2

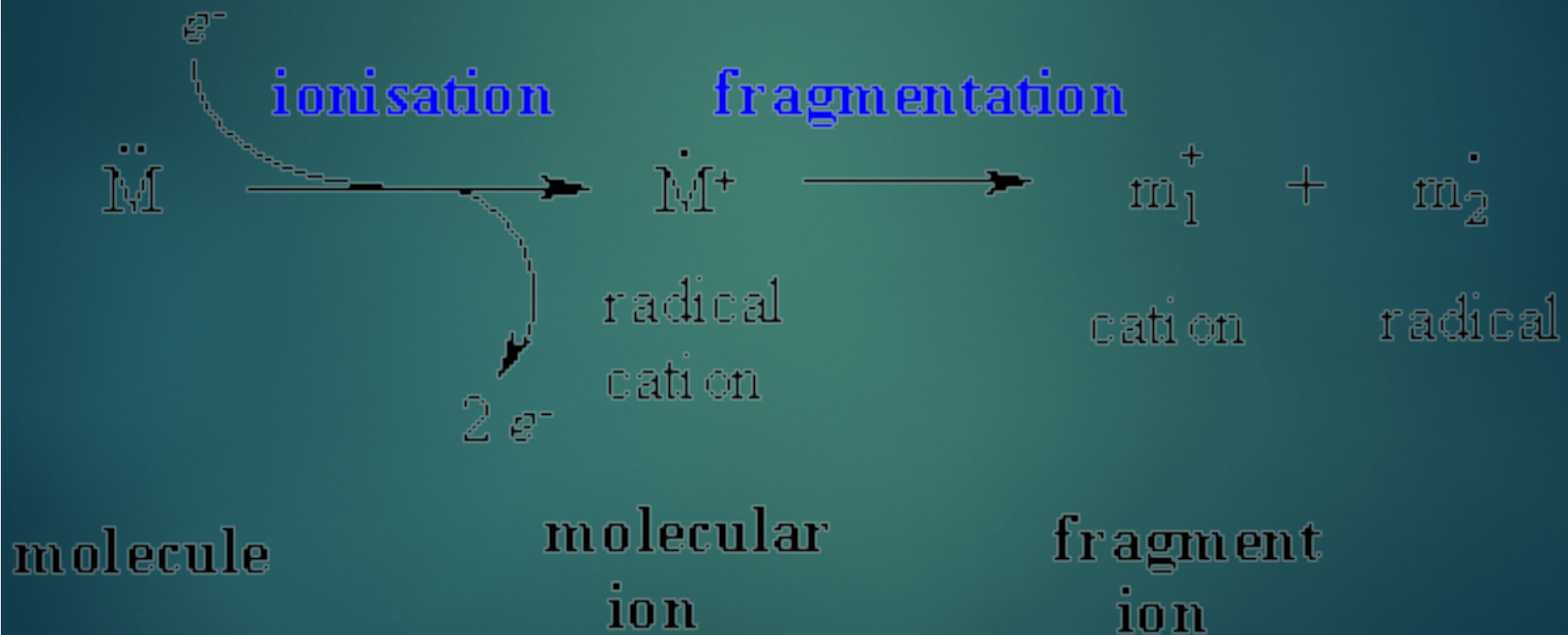
The mass spectrum of pentane, shown as a bar graph and in tabular form. The base peak represents the fragment that appears in greatest abundance. The m/z value of the molecular ion gives the molecular mass of the compound.

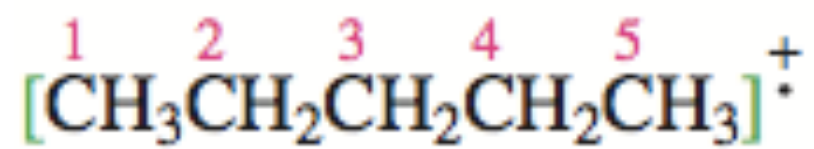
Glossário

- ▶ **Íon Molecular** – obtido a partir da perda de um e^- a partir da molécula (M^+)
- ▶ **Pico Base** – Pico mais intenso do espectro (100% intensidade)
- ▶ **Cation radical** – espécies carregadas positivamente e com número ímpar de elétrons
- ▶ **Íons Fragmentos** - cátions (cátions radicais) obtidos da decomposição do íon molecular. Geralmente são carbocátions estáveis.
- ▶ **m/z** – razão massa carga

Ionização – Formação de cátion-radical

Ion Molecular (M^+)

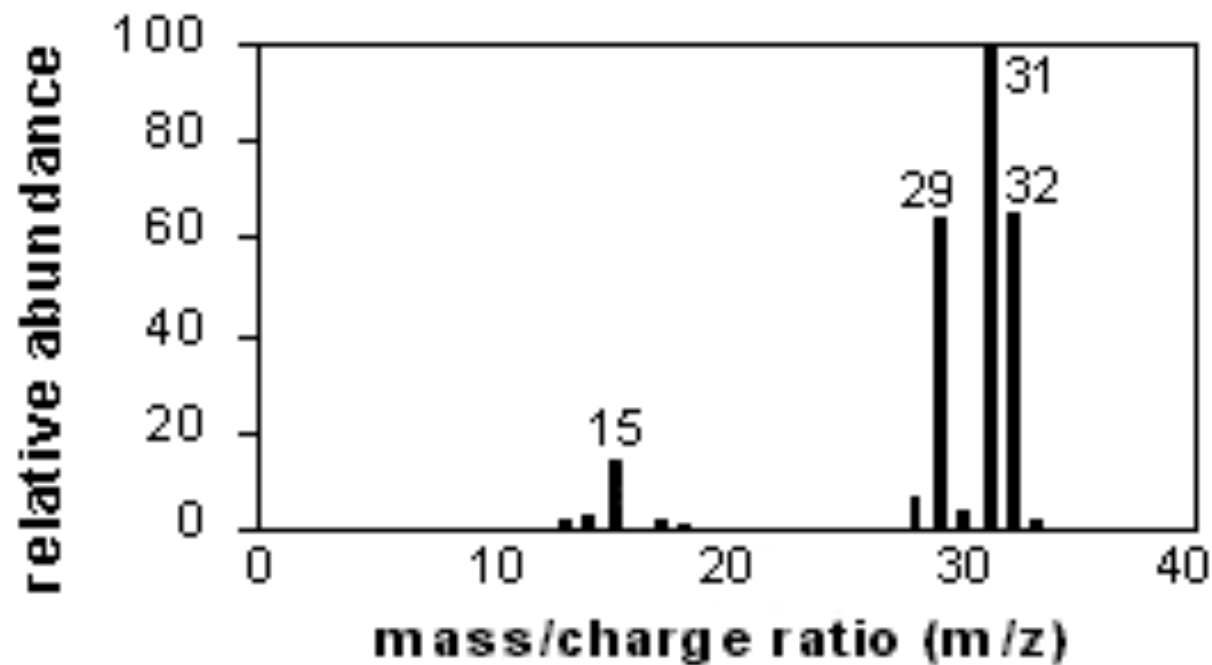




molecular ion

$$m/z = 72$$

Metanol



ions	m/z
$\text{CH}_3\text{OH}^{+\bullet}$	32
$\text{H}_2\text{C}=\text{OH}^+$	31
$\text{HC}\equiv\text{O}^+$	29
H_3C^+	15

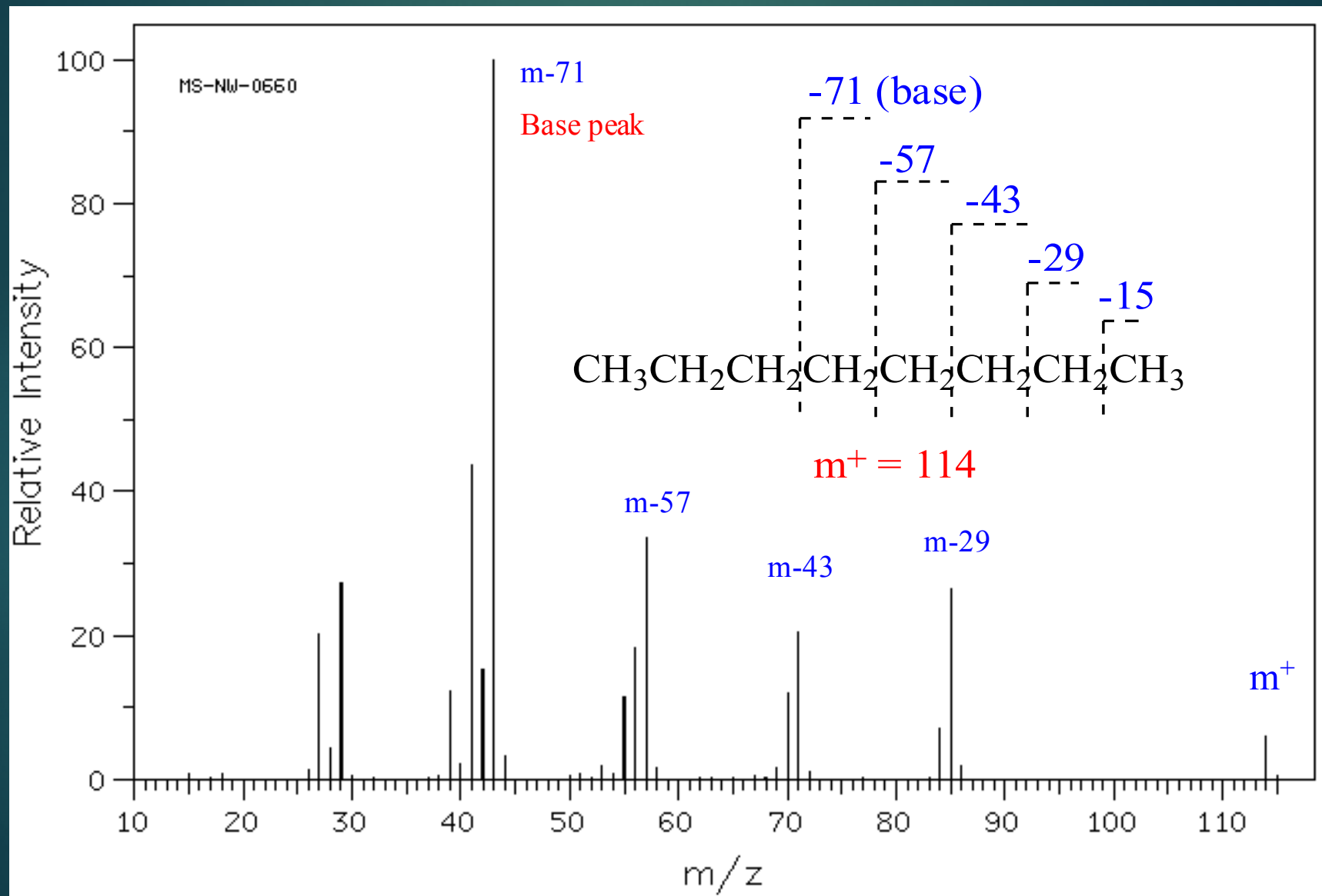
Espectrômetros de massas de baixa resolução

- ▶ Massa molecular nominal dos fragmentos (massa mais próxima de um número inteiro)

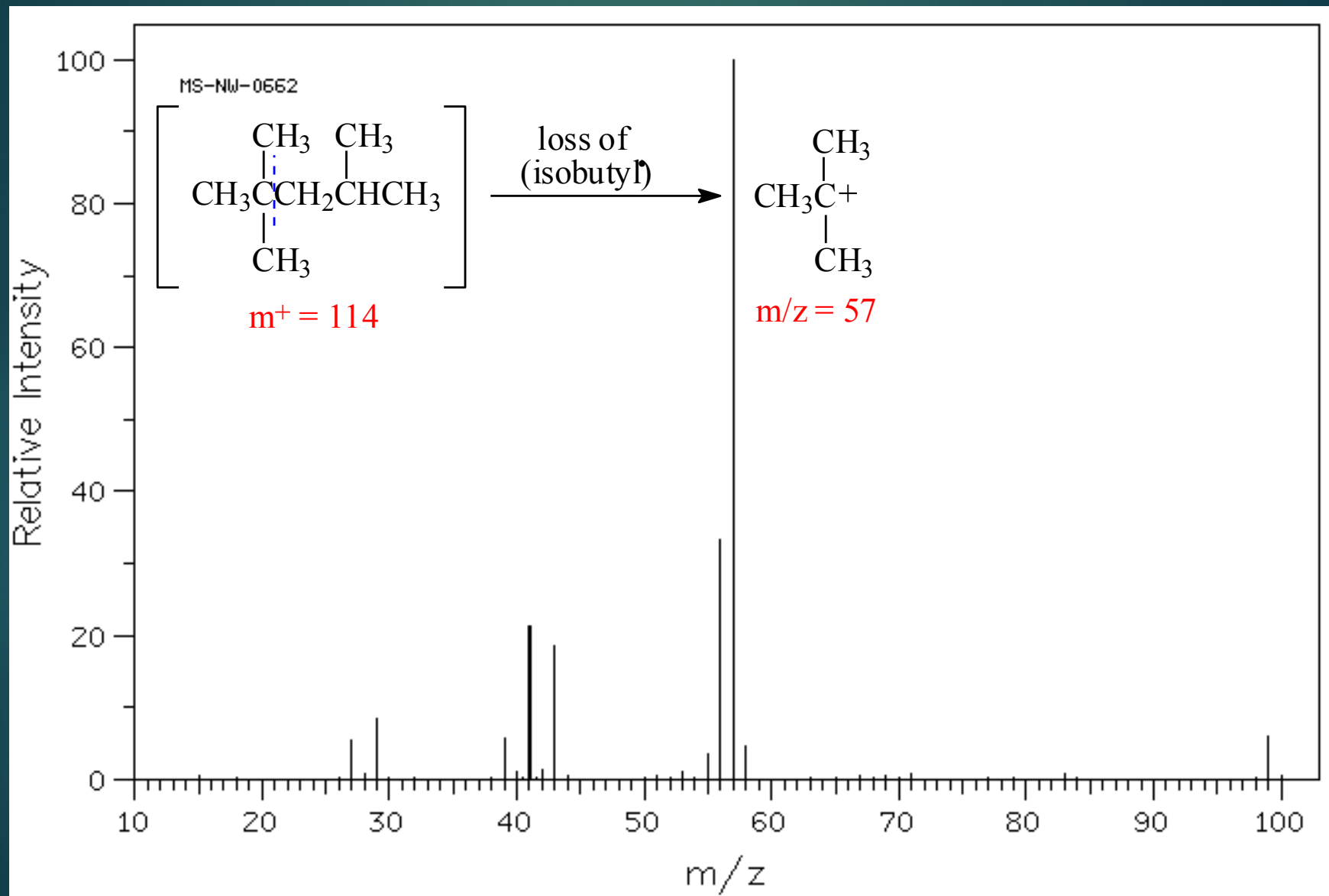
Massas de alta resolução pode determinar a massa molecular exata de um fragmento com precisão de até 0,0001 uma.

Molecular formula	C₉H₁₄	C₇H₁₀N₂	C₈H₁₀O	C₇H₆O₂	C₄H₁₀O₄	C₄H₁₀S₂
Exact molecular mass (amu)	122.1096	122.0845	122.0732	122.0368	122.0579	122.0225

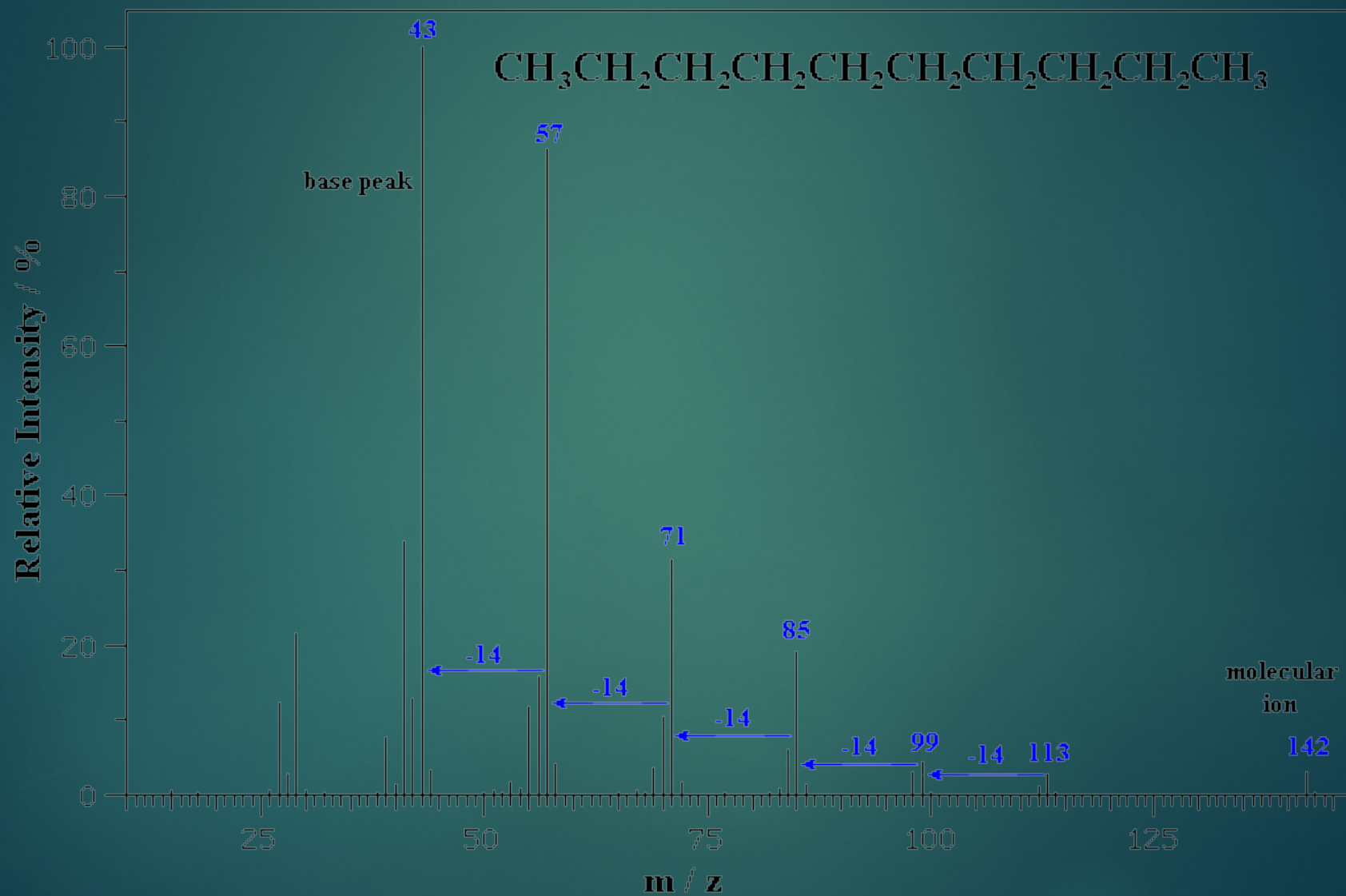
Octano, $M^+ = 114$



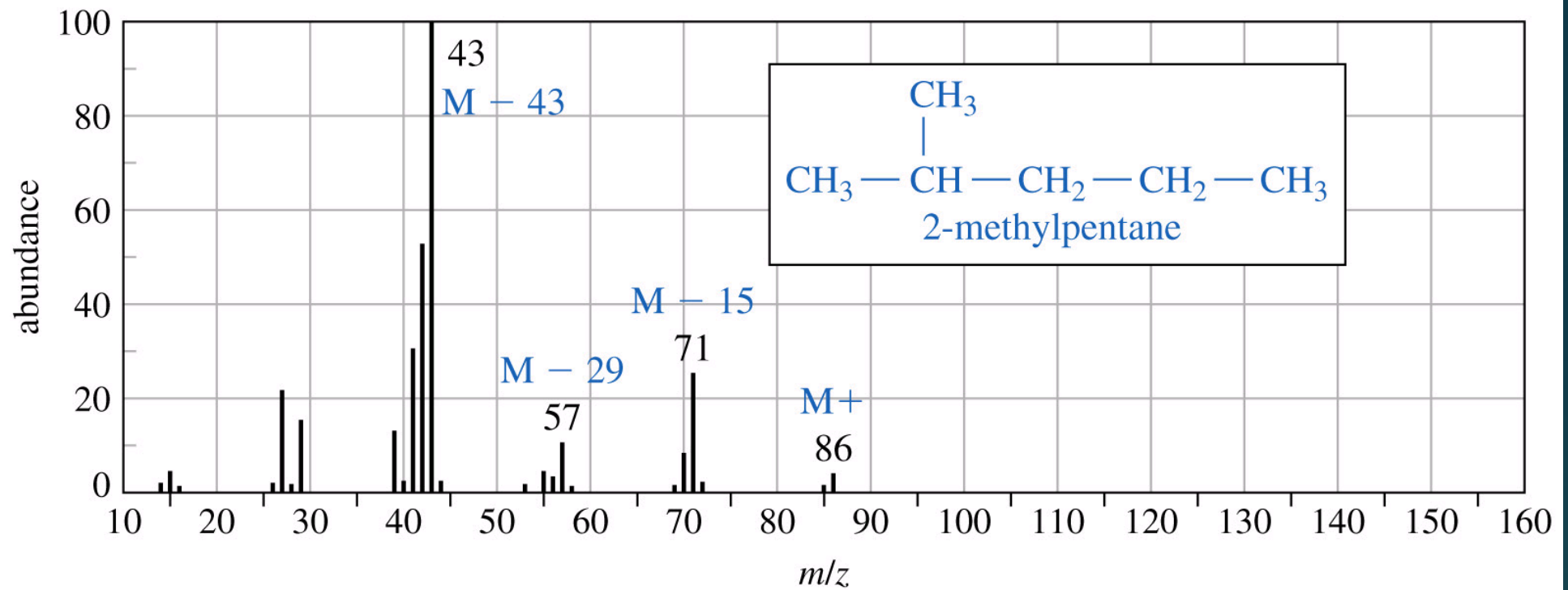
Isooctano, Não apresenta íon molecular



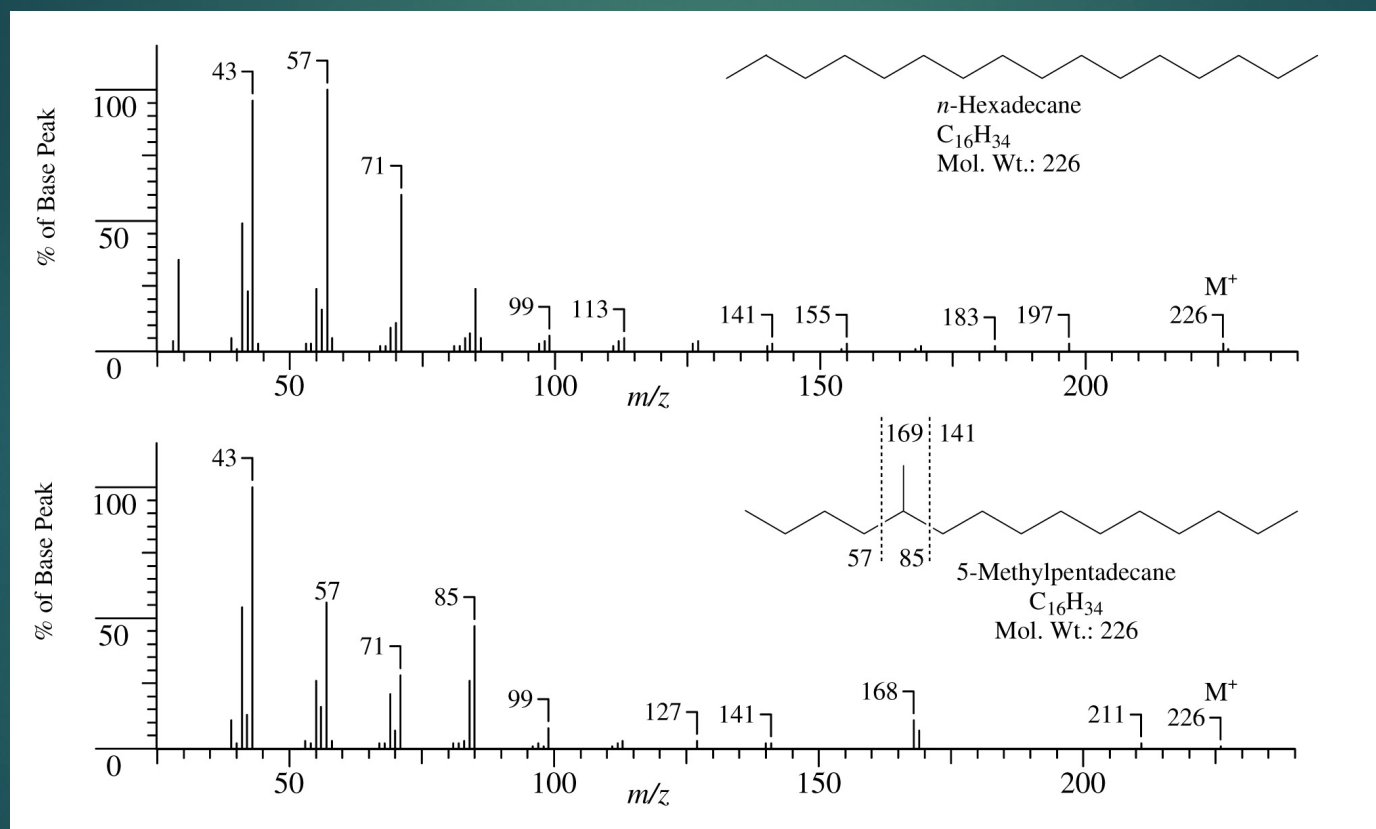
Decano



2-Metilpentano



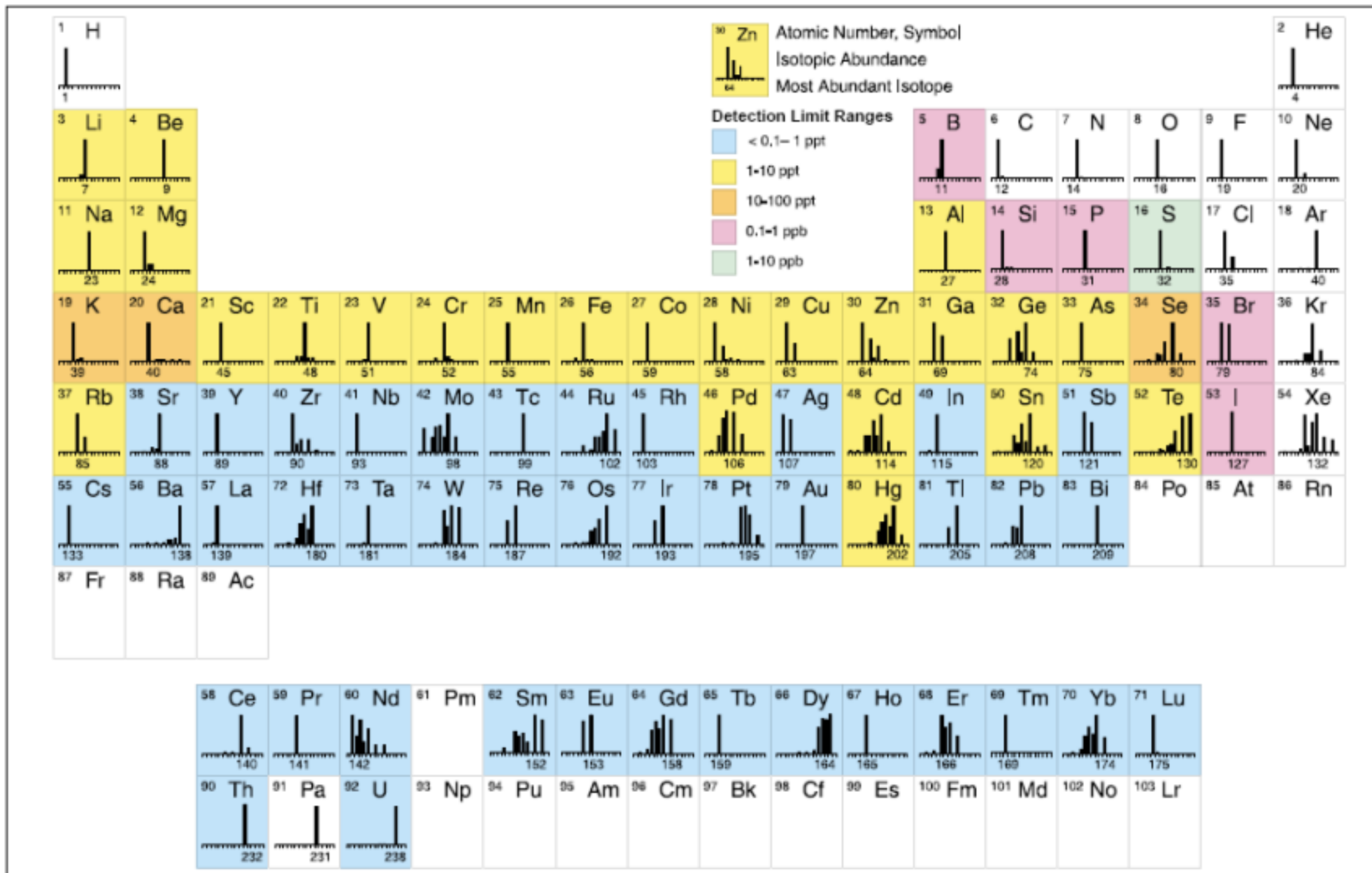
Espectro de massas de isômeros



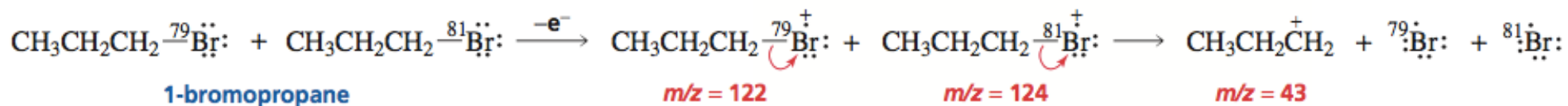
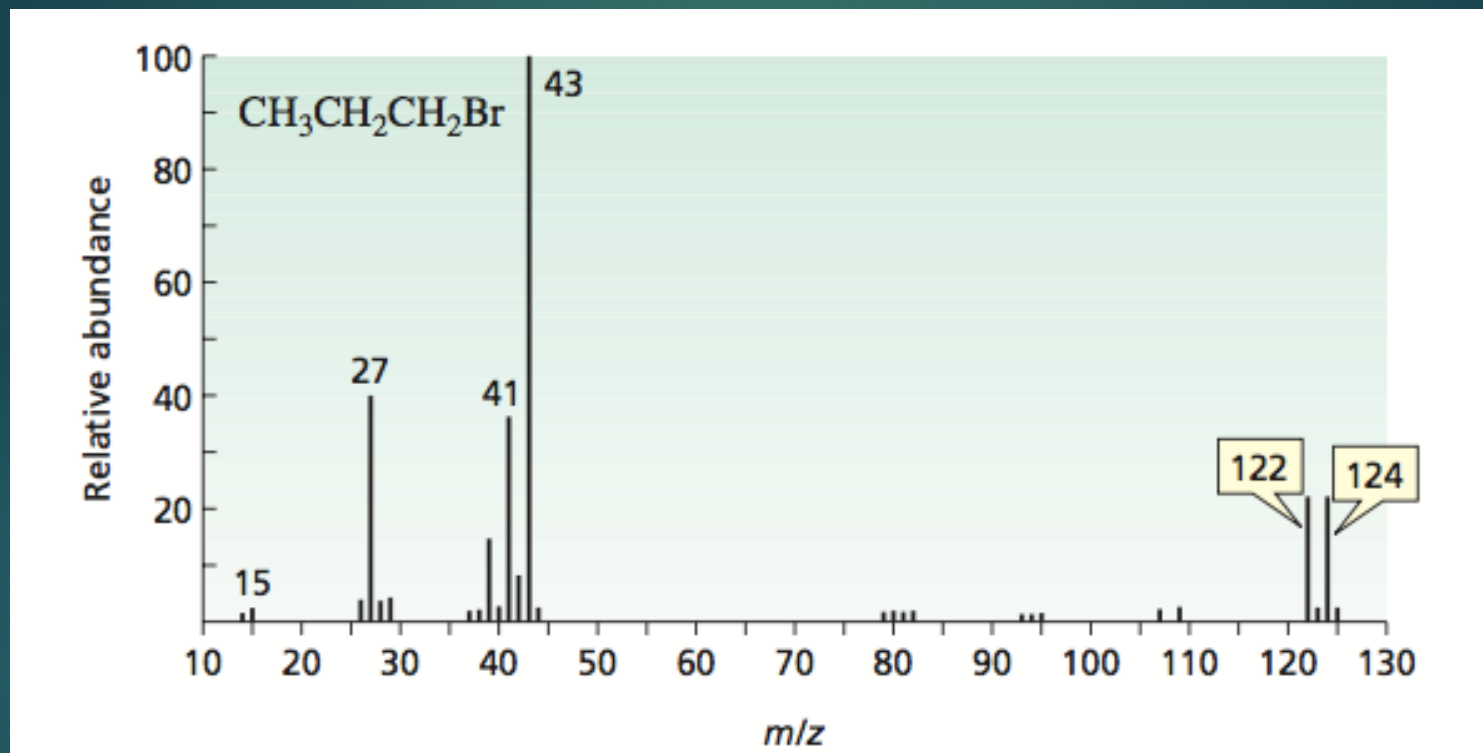
Isótopos

- ▶ Moléculas contendo diferentes isótopos podem ser identificados e distinguidos.
- ▶ No caso de Bromo ou Cloro ($^{79}\text{Br} : ^{81}\text{Br}$, intensidade 1:1 e $^{35}\text{Cl} : ^{37}\text{Cl}$, intensidade 3:1). Assim serão observados os picos "M" e "M+2".
- ▶ A intensidade estará associada à abundância natural destes isótopos.
- ▶ Picos de "M+1" pode ser visto devido a presença de ^{13}C na amostra.

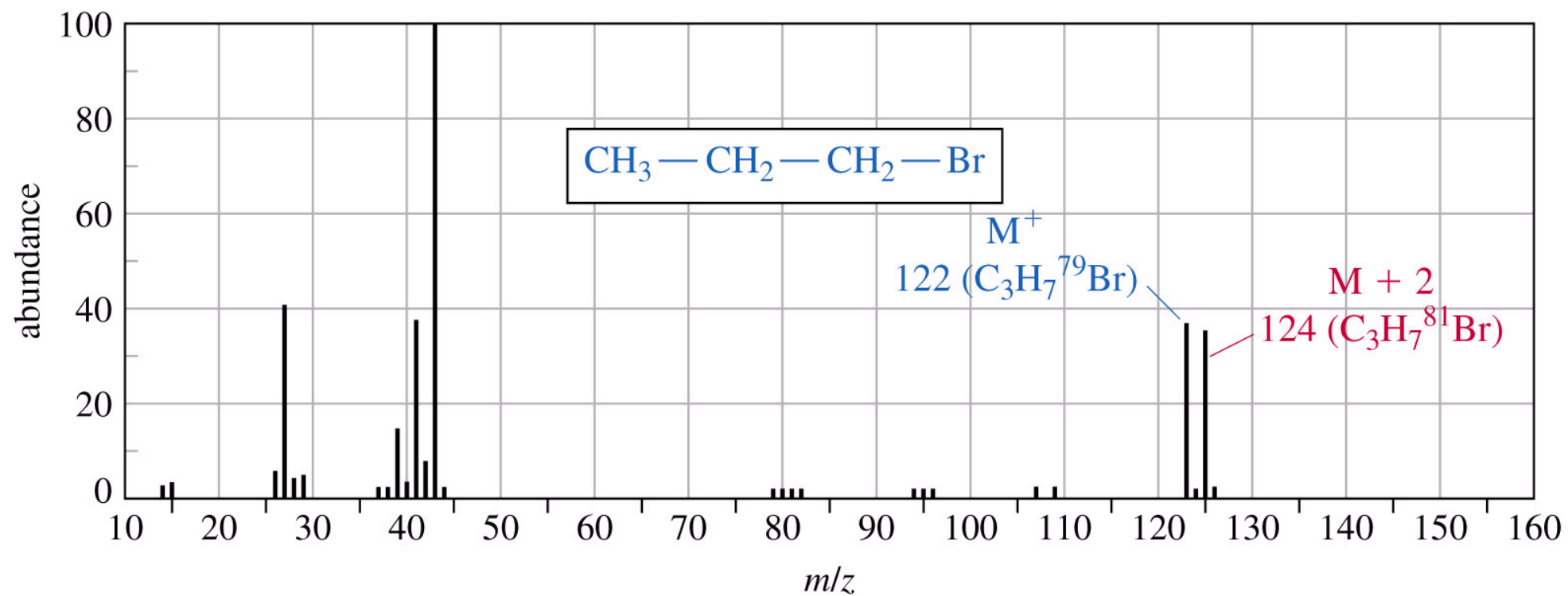
Isotopos na Espectroscopia de Massa

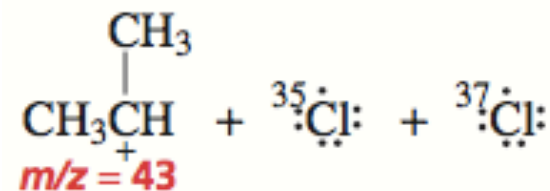
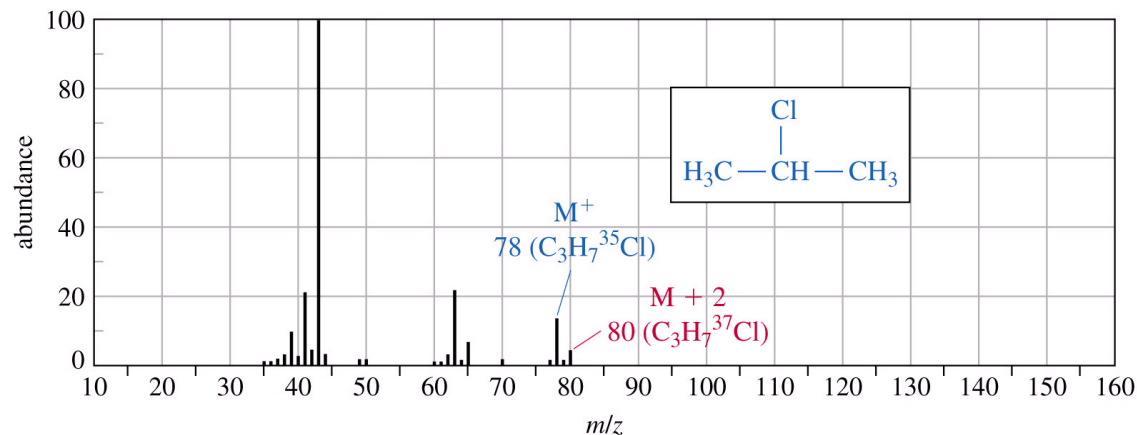


1-bromopropano

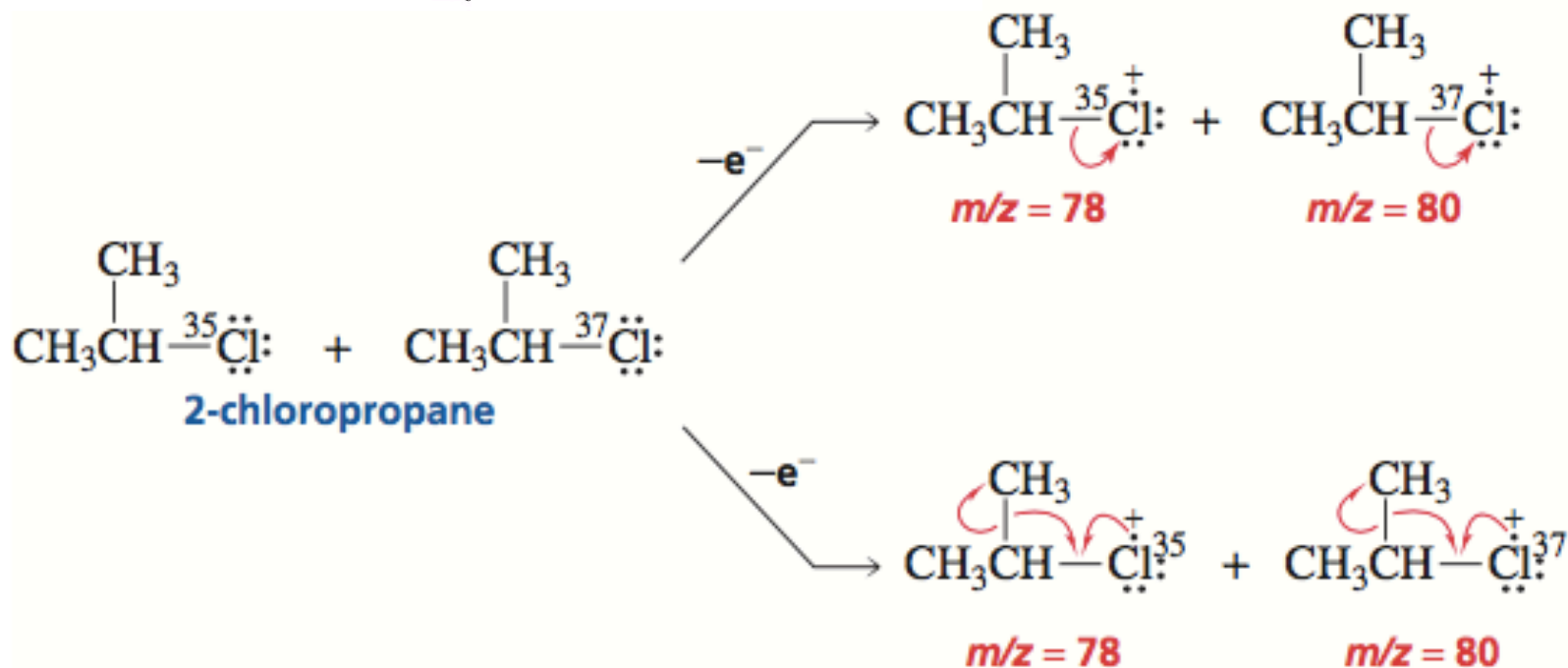


1-Bromopropano

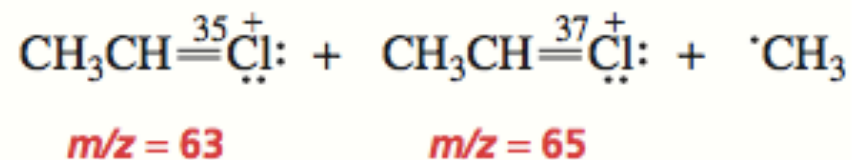




↑ heterolytic cleavage

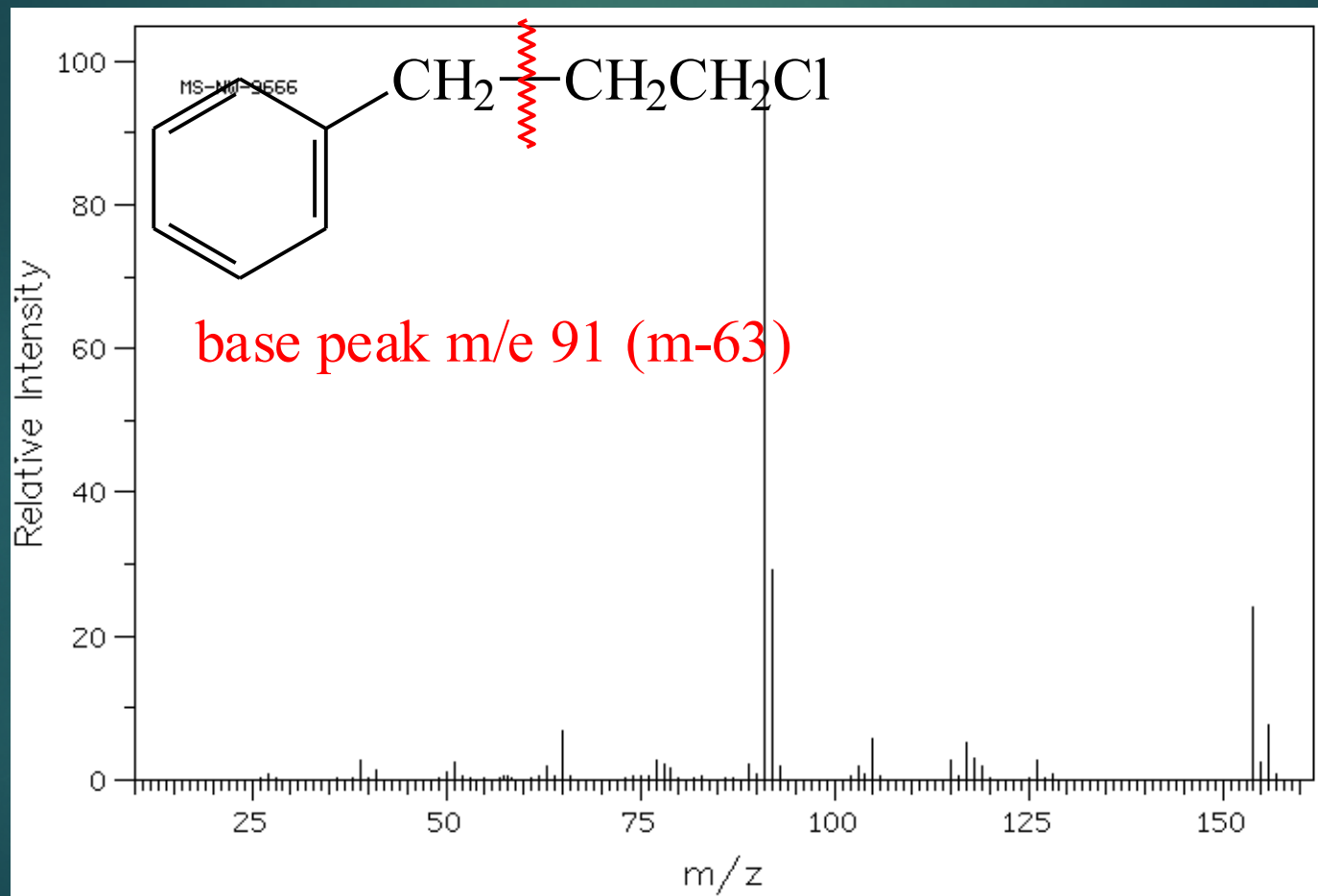


↓ homolytic cleavage



2-Chloropropano

(3-Cloropropil)benzeno

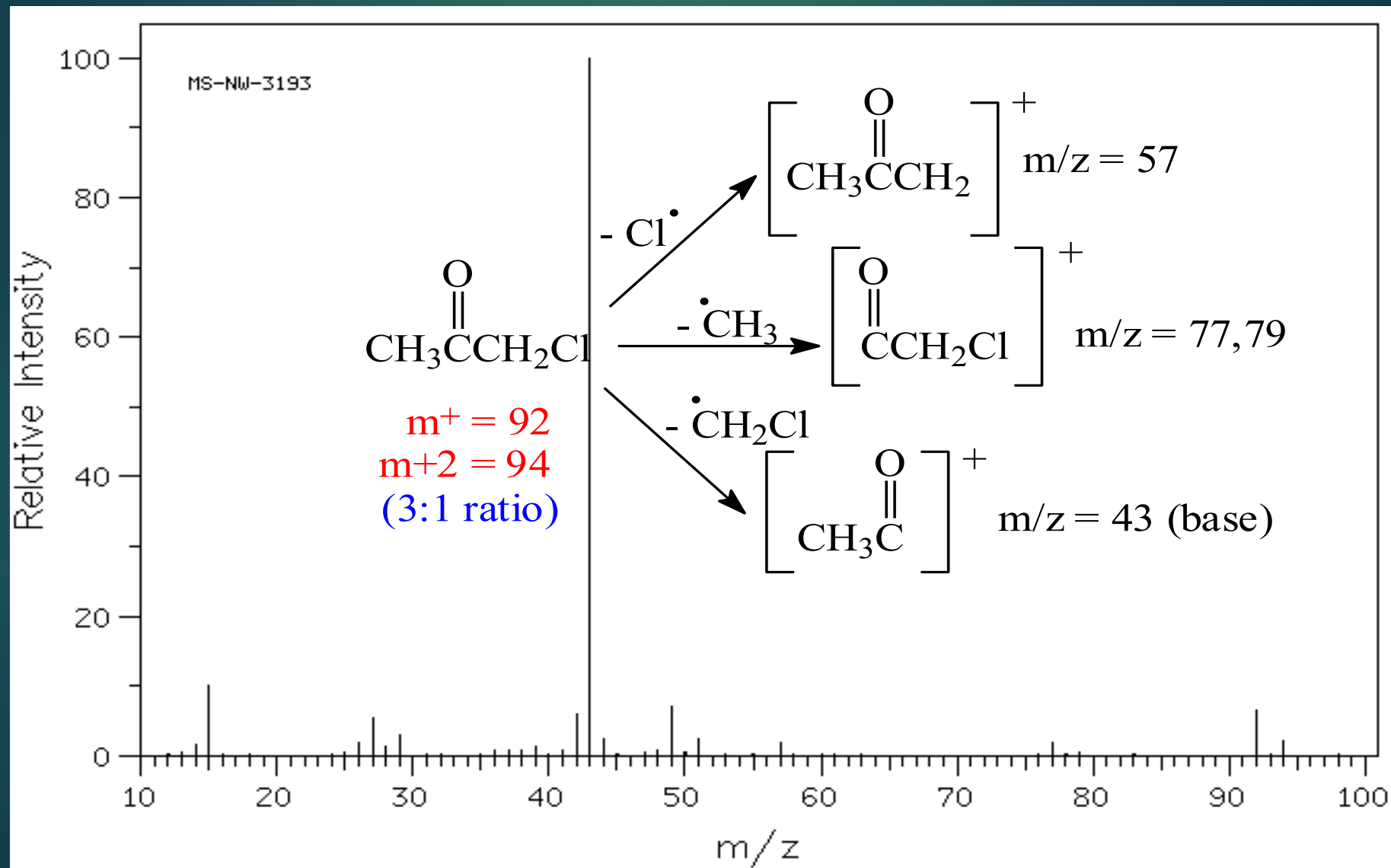


Isótopos na espectrometria de massas

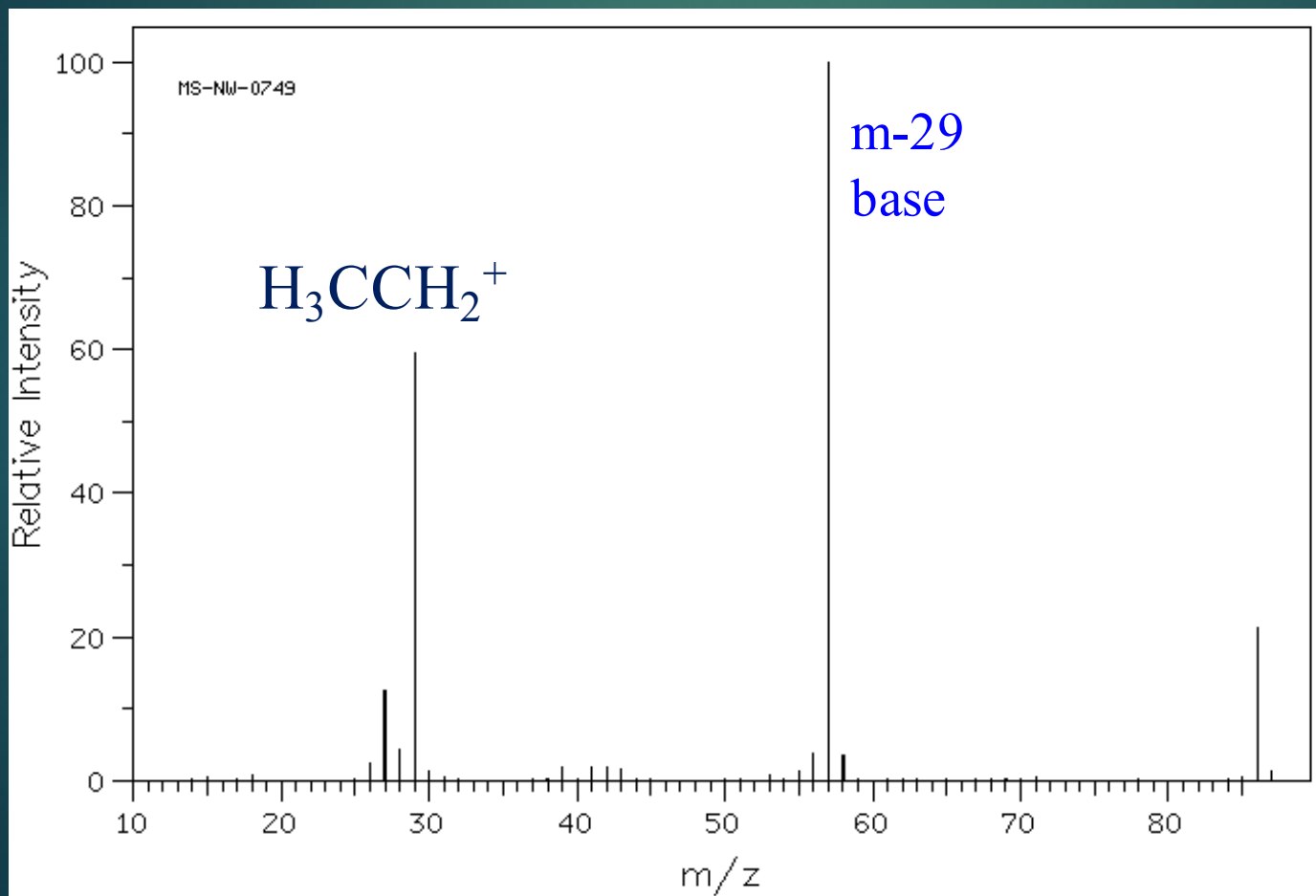
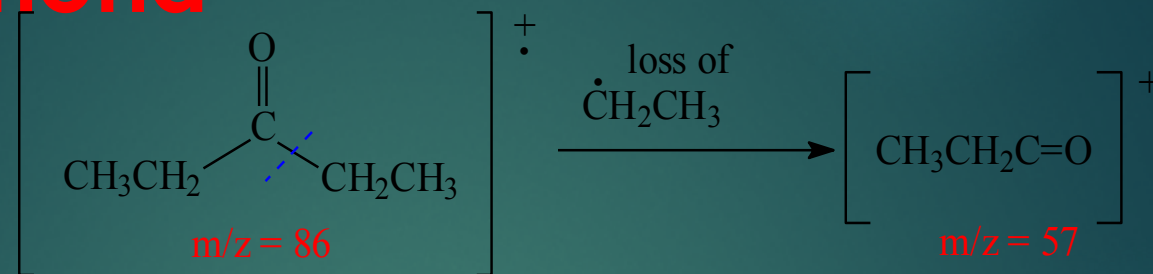
- ▶ Abundância natural dos isótopos pode auxiliar na identificação da amostra

$$\text{number of carbon atoms} = \frac{\text{relative intensity of } M + 1 \text{ peak}}{.011 \times (\text{relative intensity of } M \text{ peak})}$$

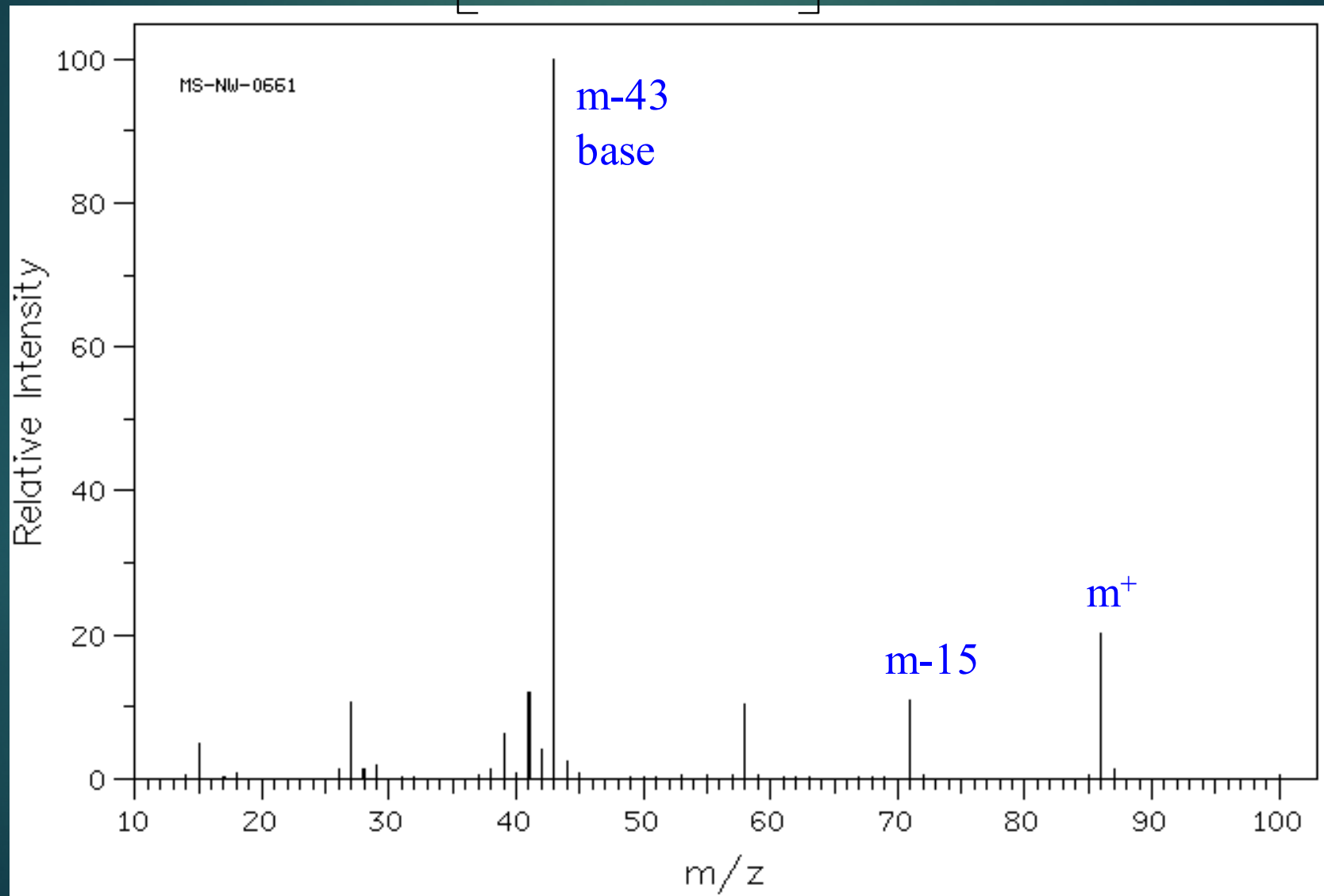
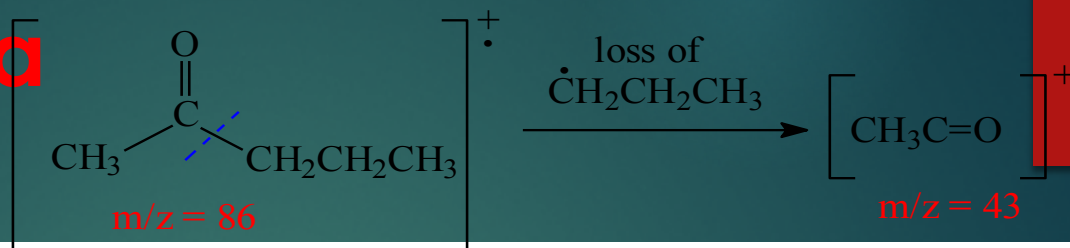
Cloroacetona



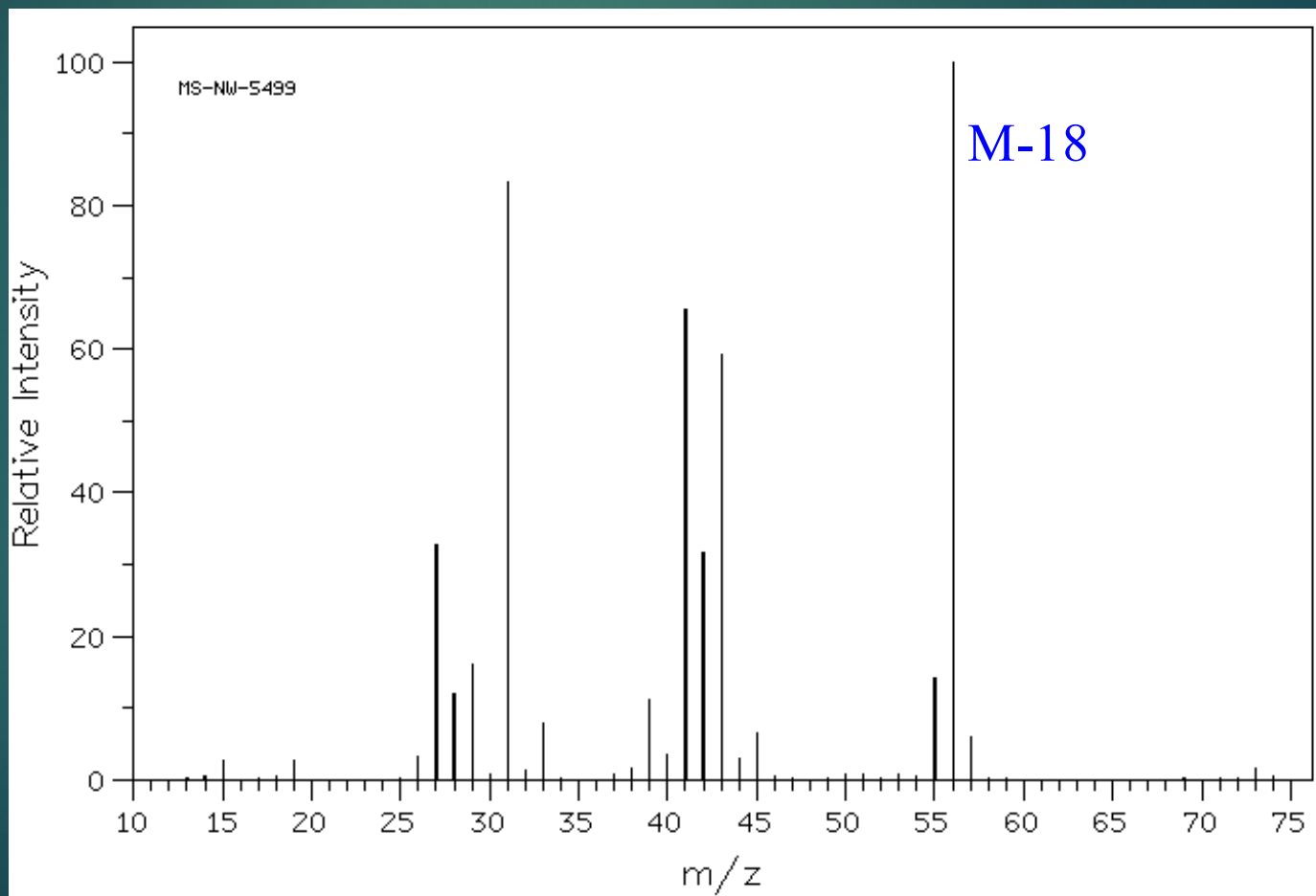
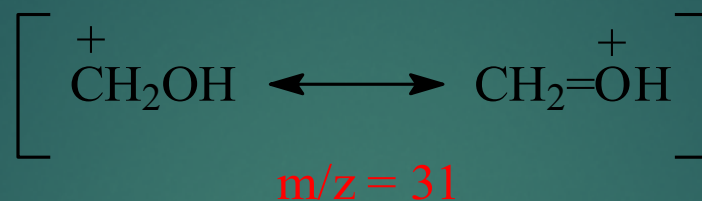
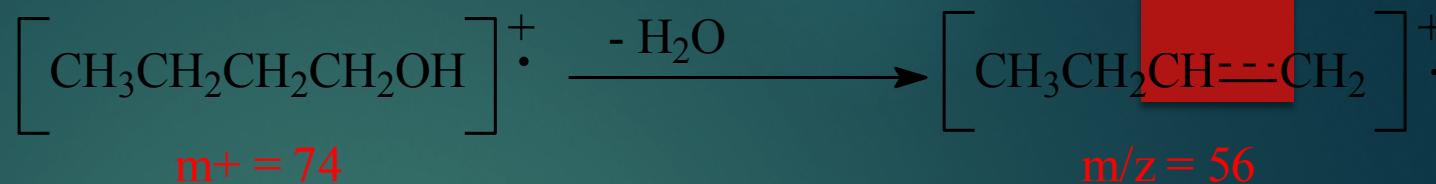
3-Pentanona



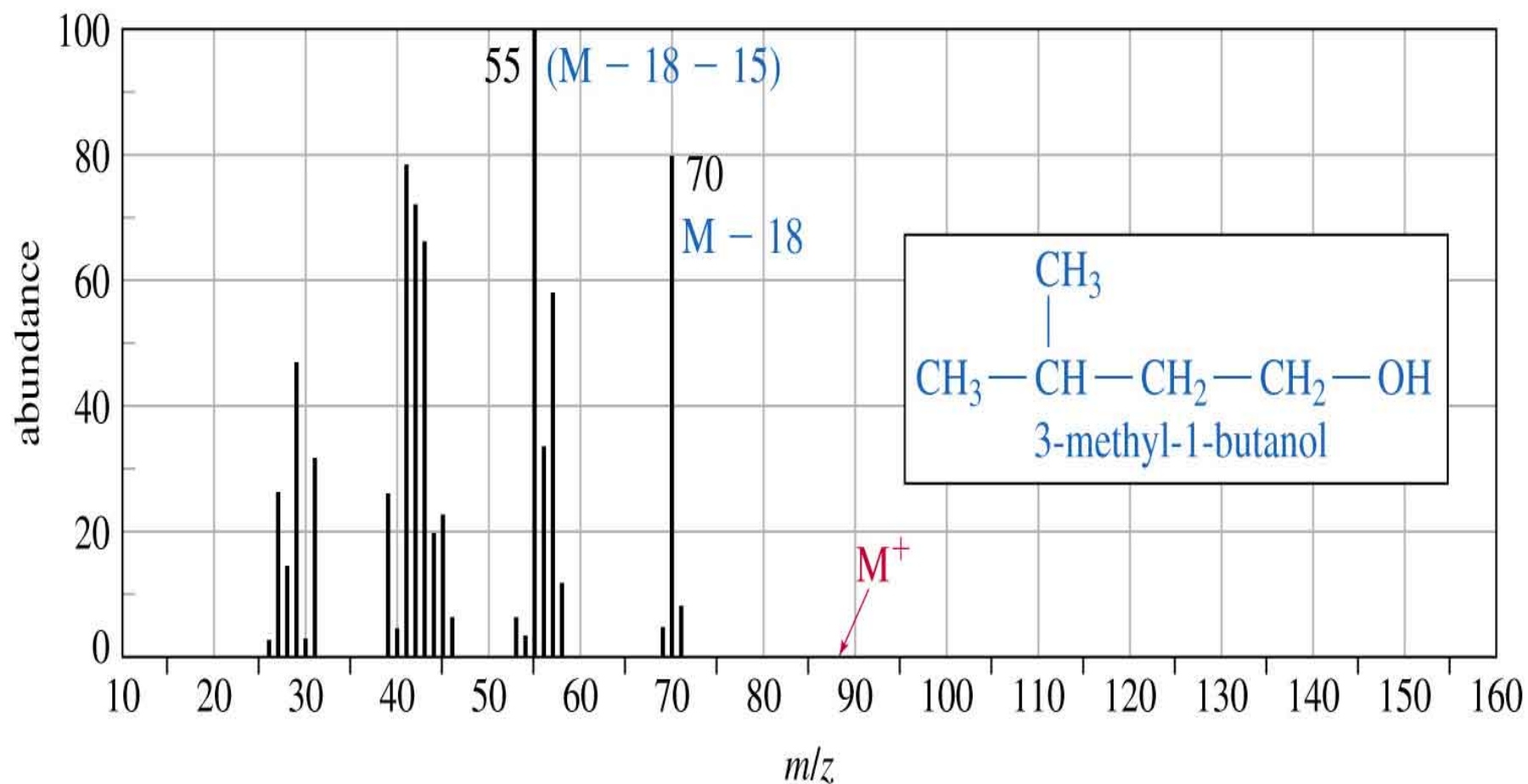
2-Pentanone



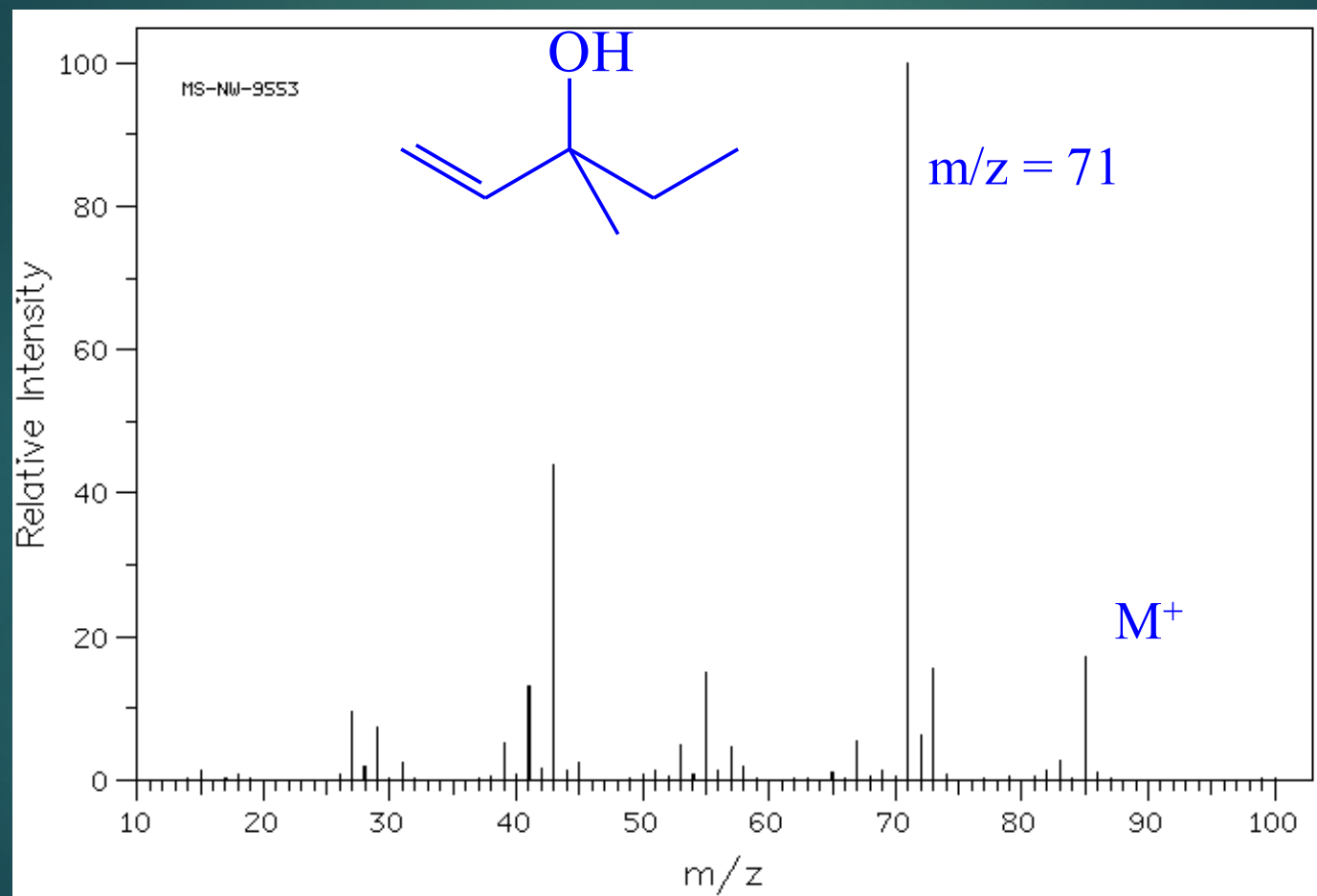
1-Butanol



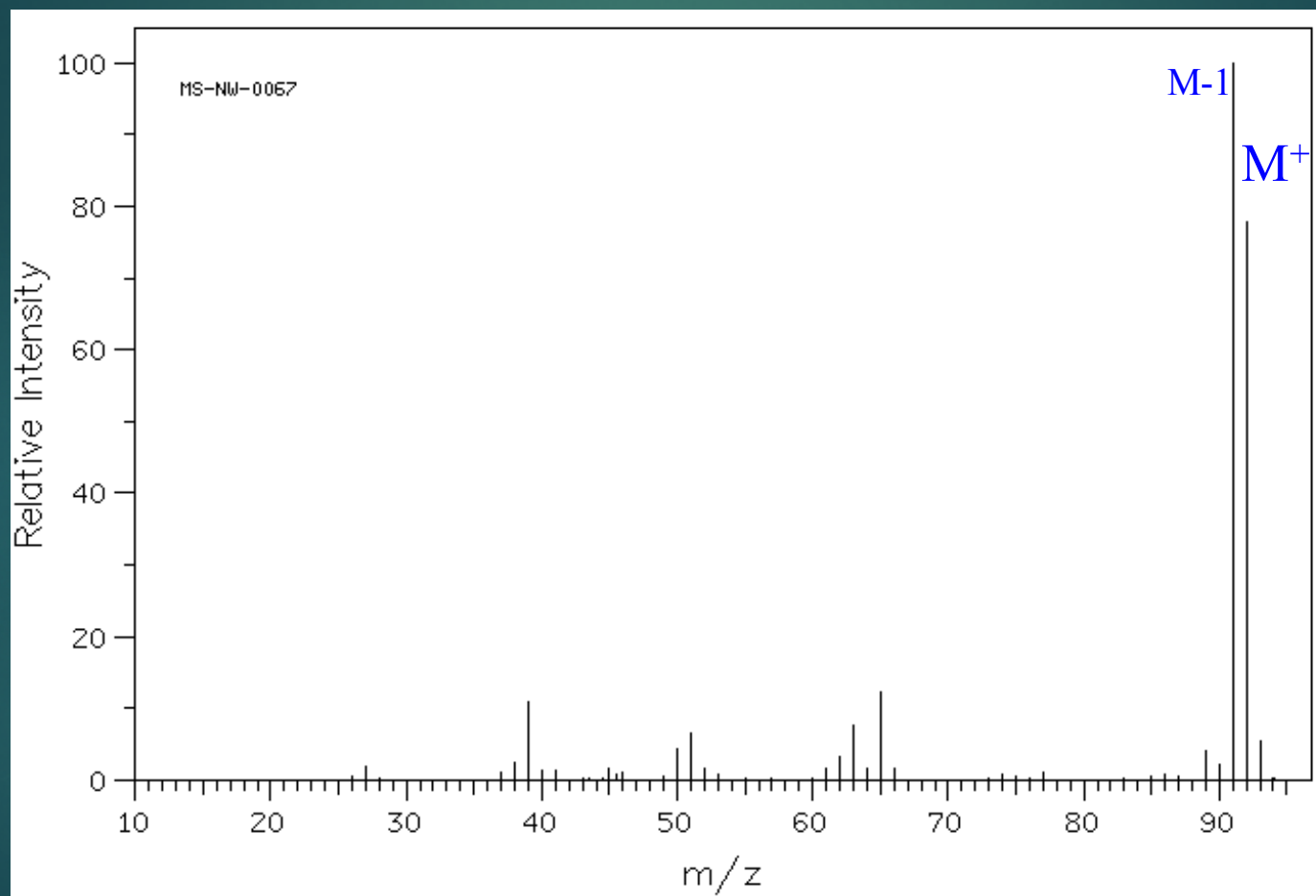
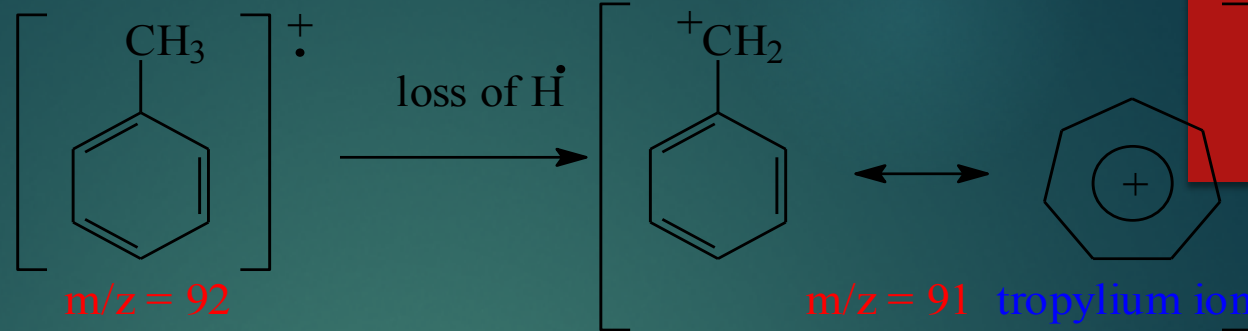
1° Alcool: Perda de molécula de H₂O



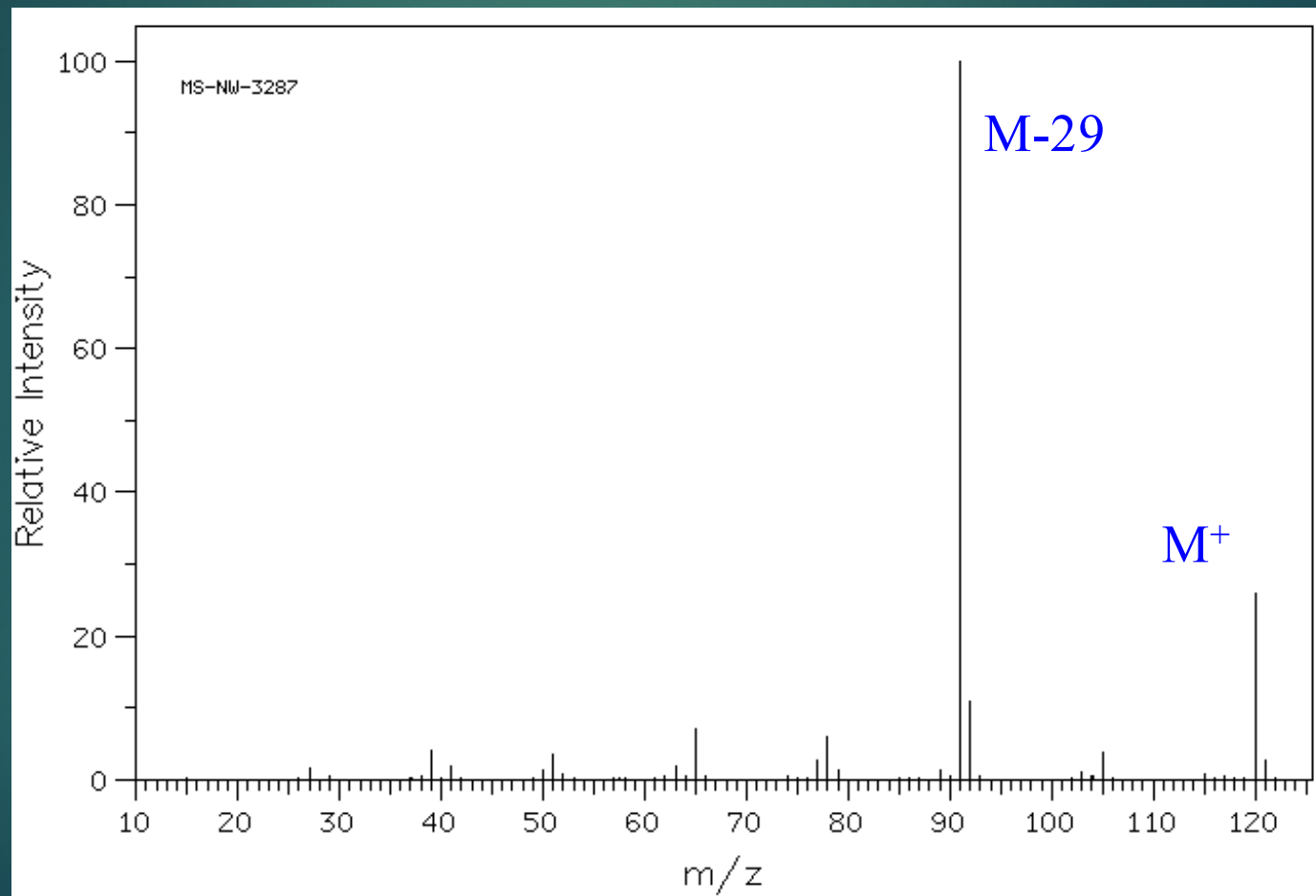
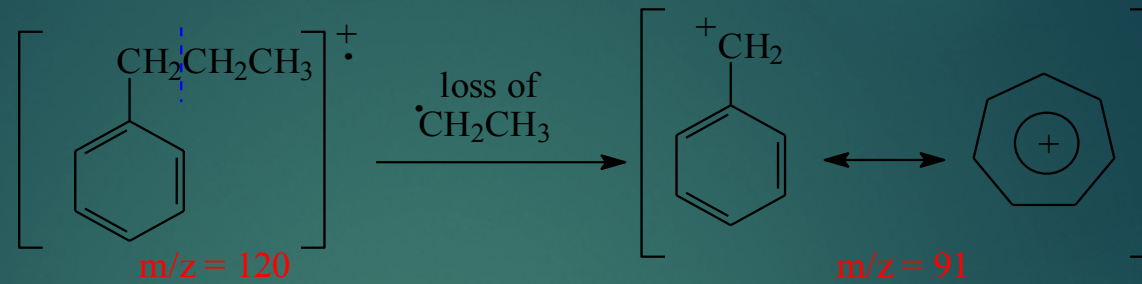
3-Metil-1-penten-3-ol



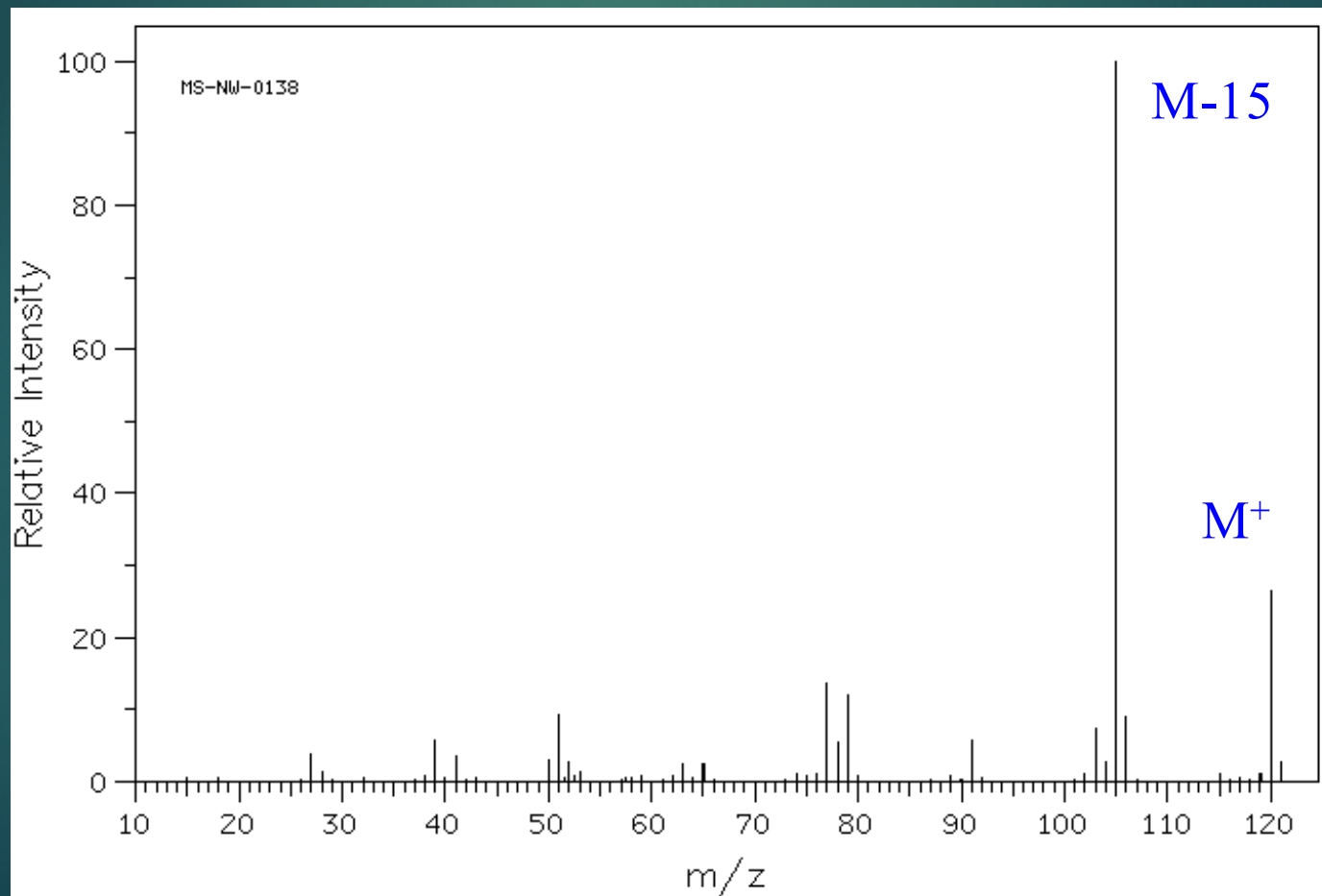
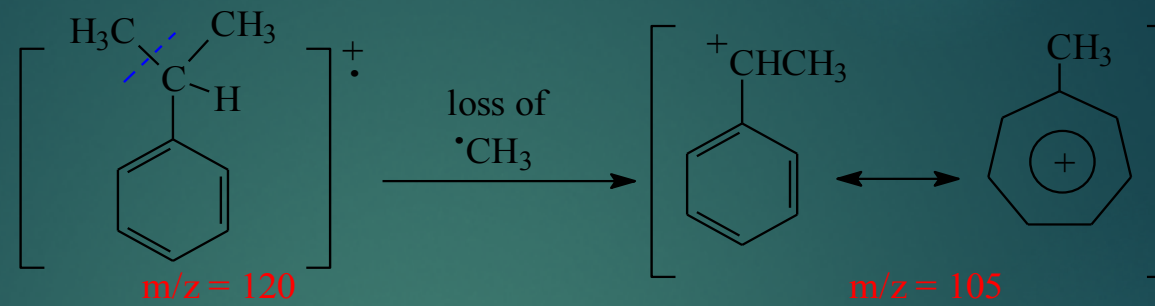
Tolueno



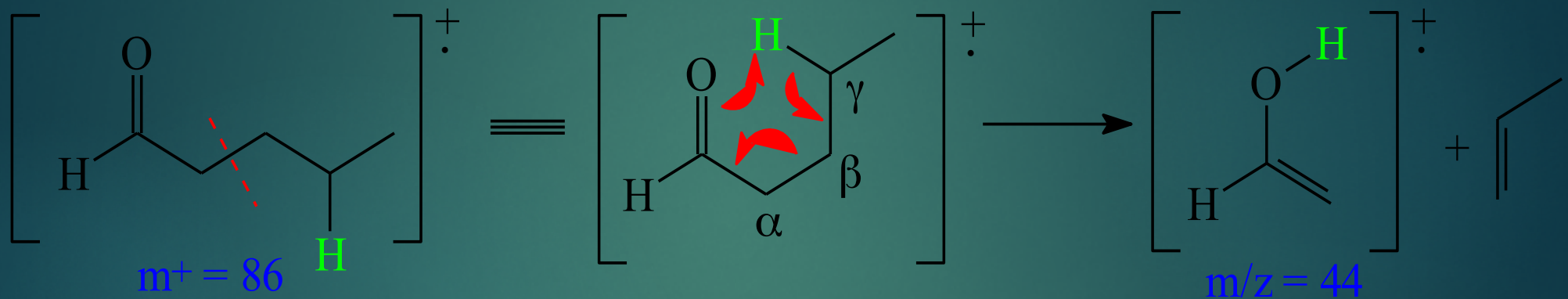
Propilbenzeno



Isopropilbenzeno

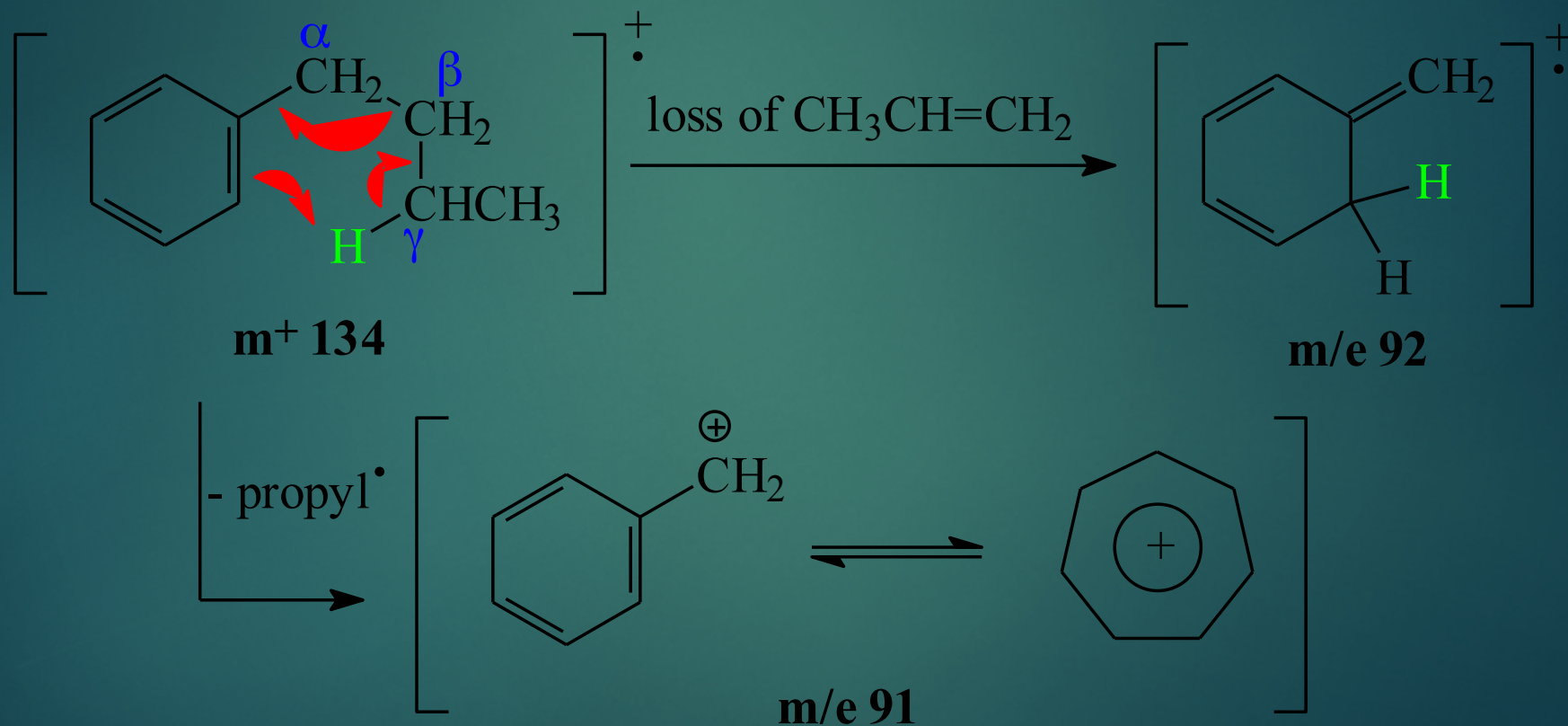


Rearranjo de McLafferty



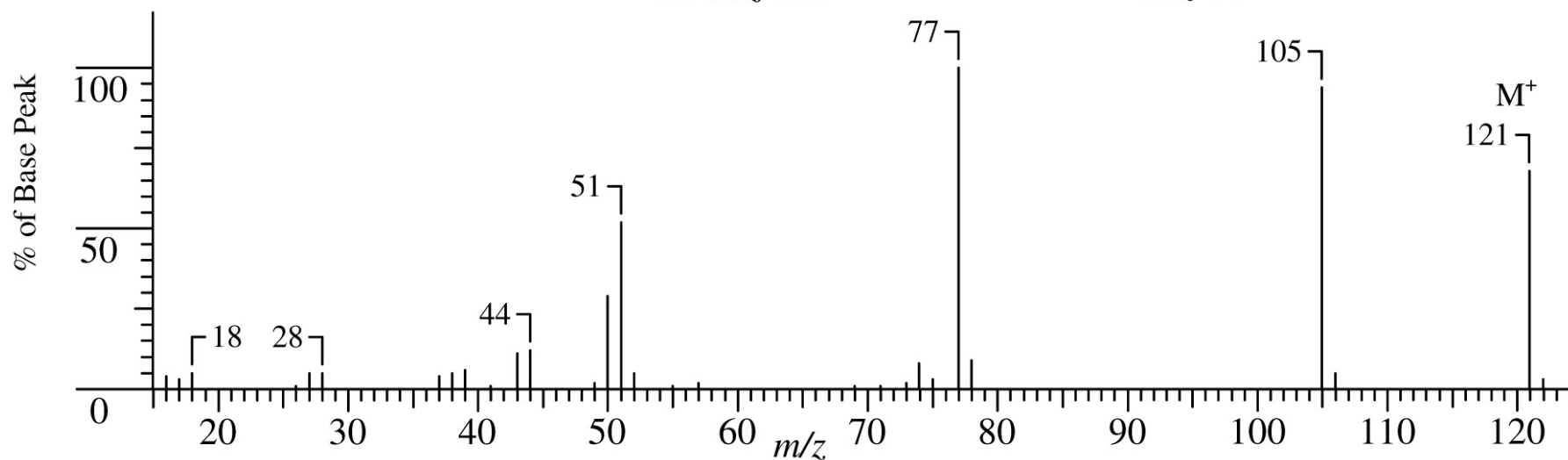
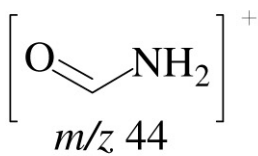
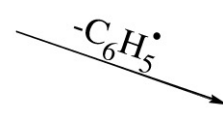
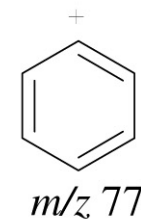
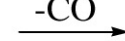
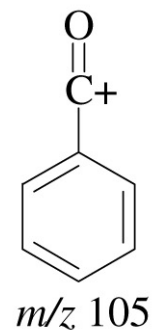
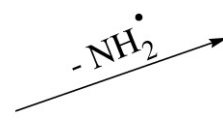
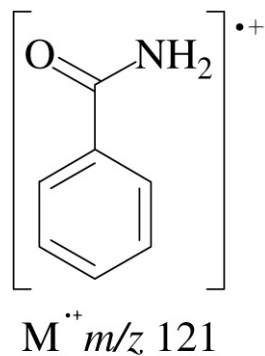
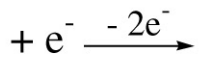
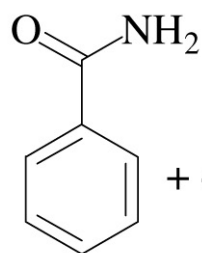
Transferência de H de um carbono situado a 3 carbonos da carbonila e elimina um alceno neutro

Rearranjo de McLafferty em alquil benzenos

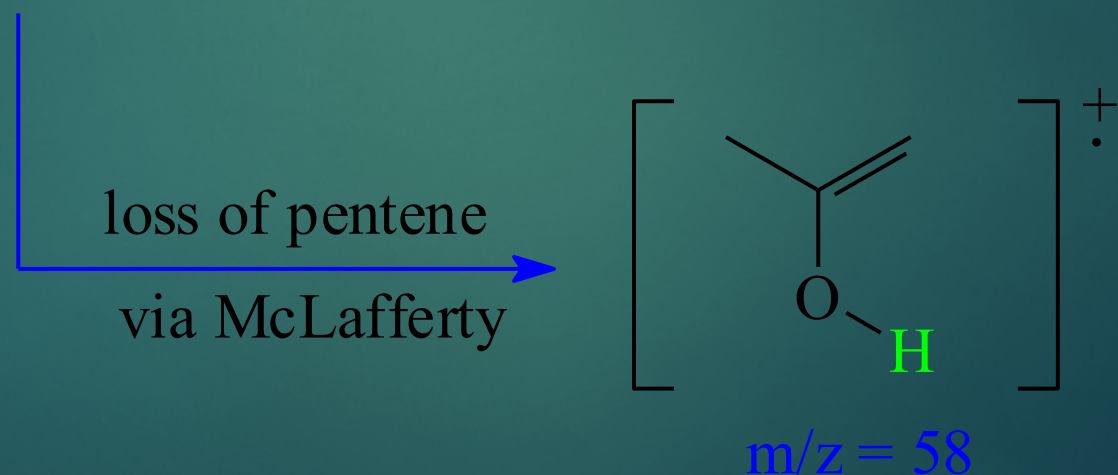
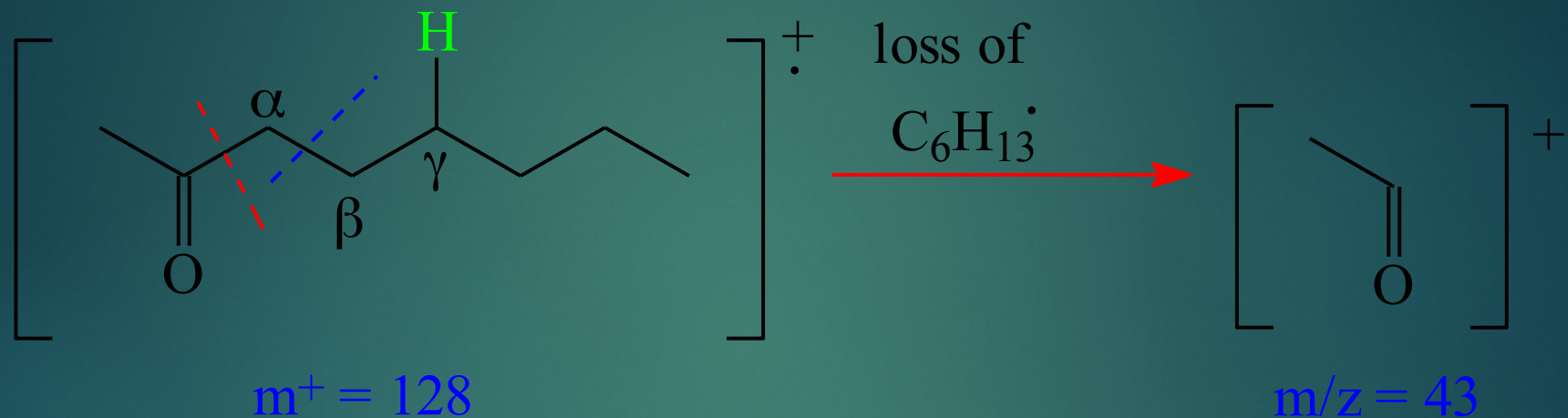


Benzamida

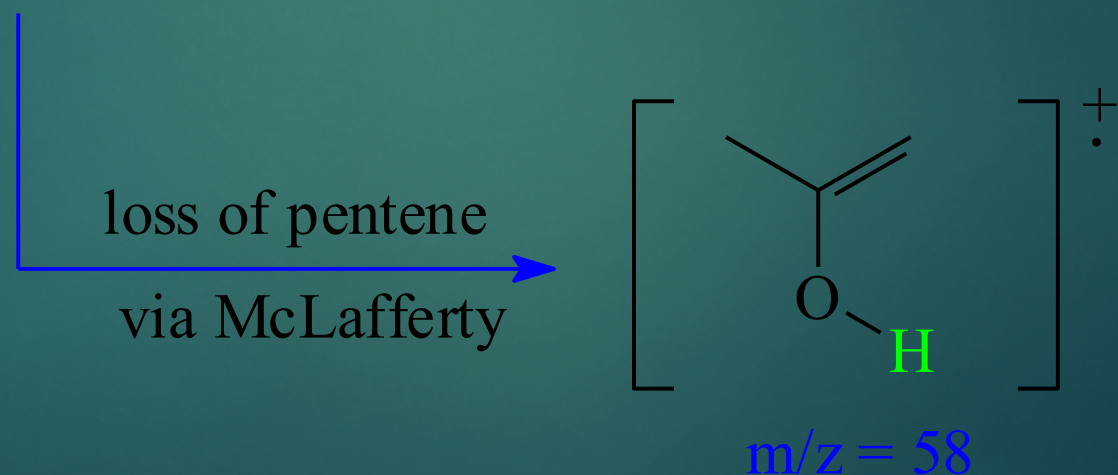
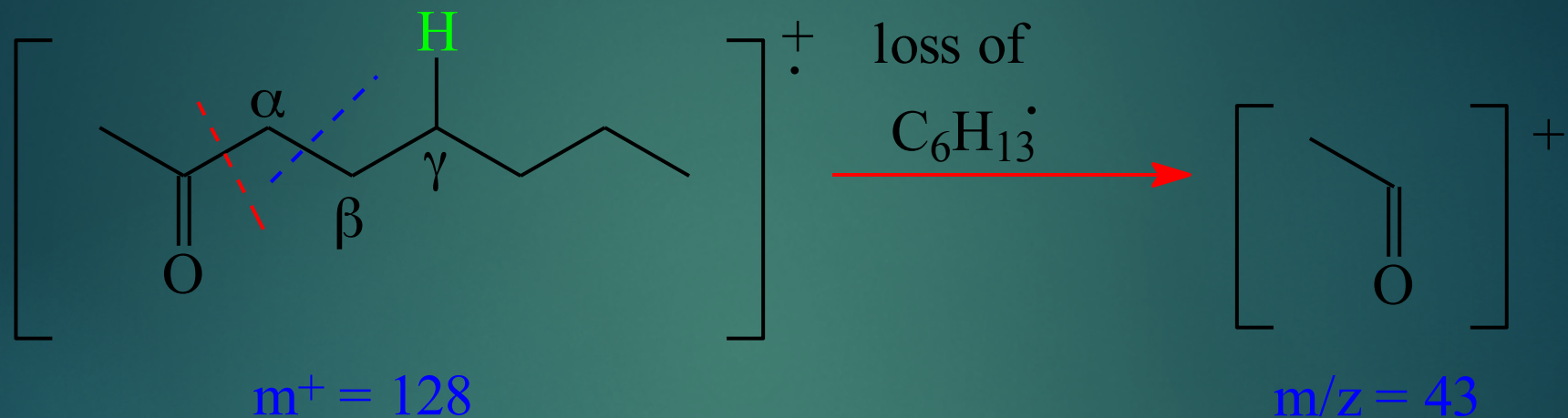
Benzamide
 C_7H_7NO
Mol. Wt.: 121



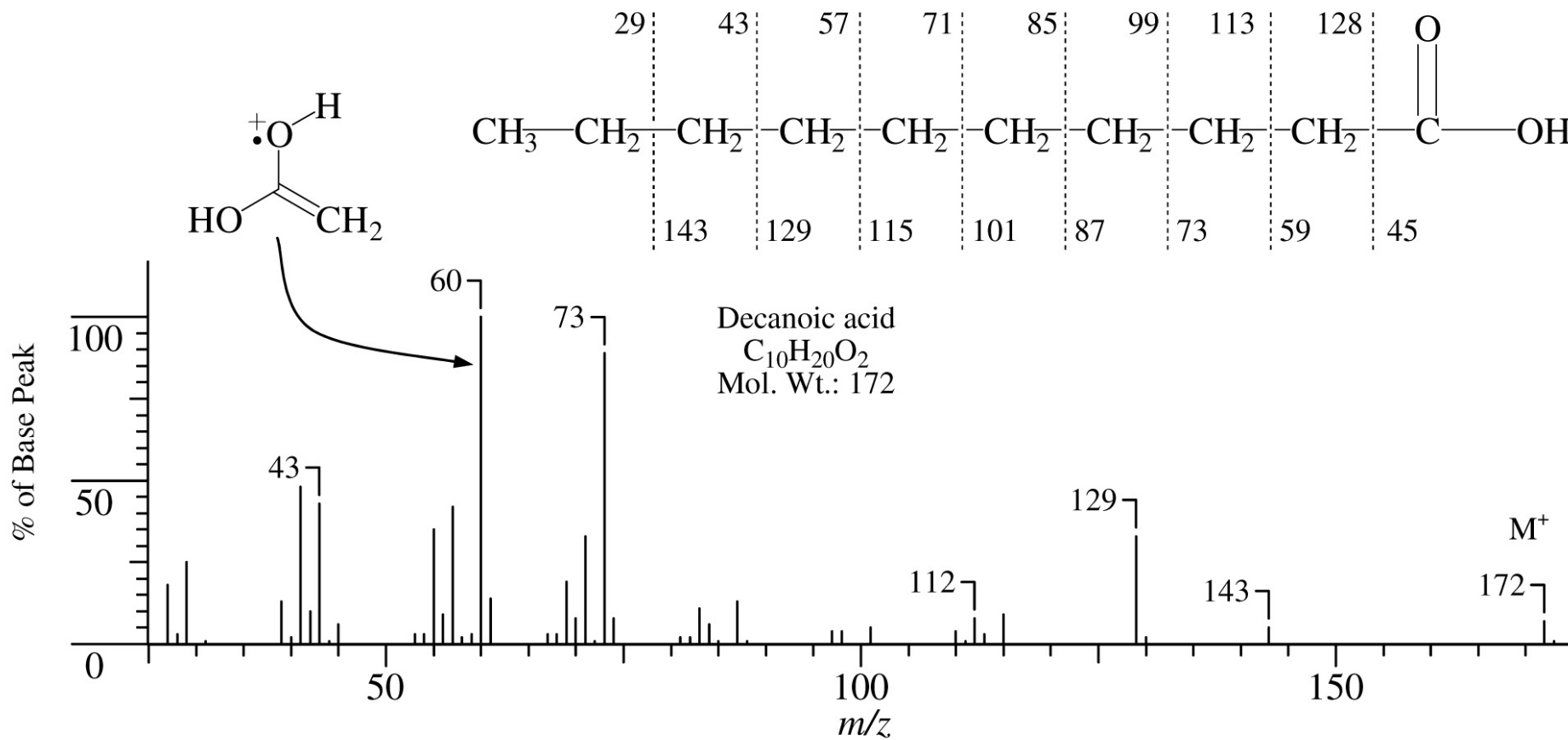
2-Octanona



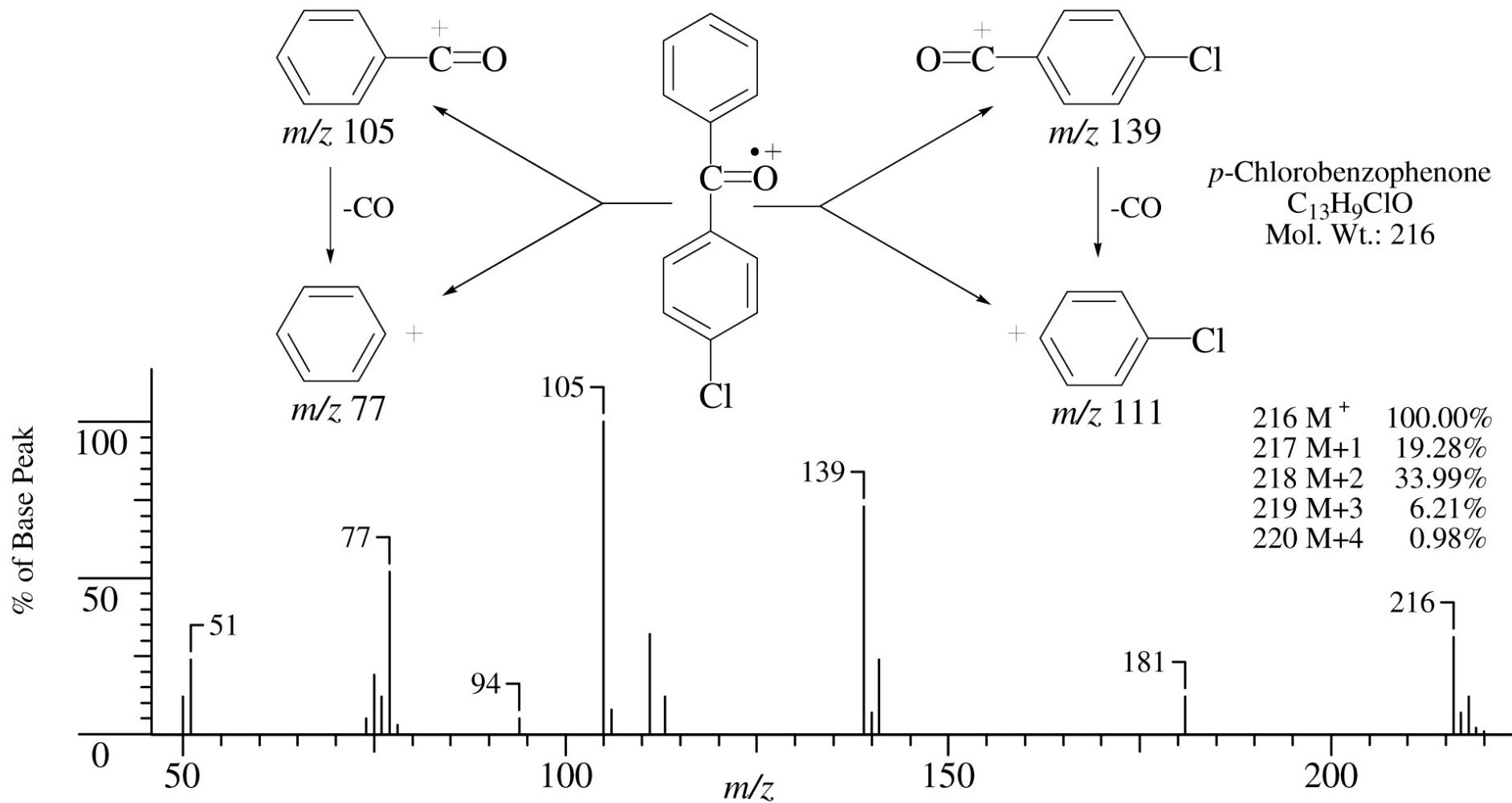
2-Octanona



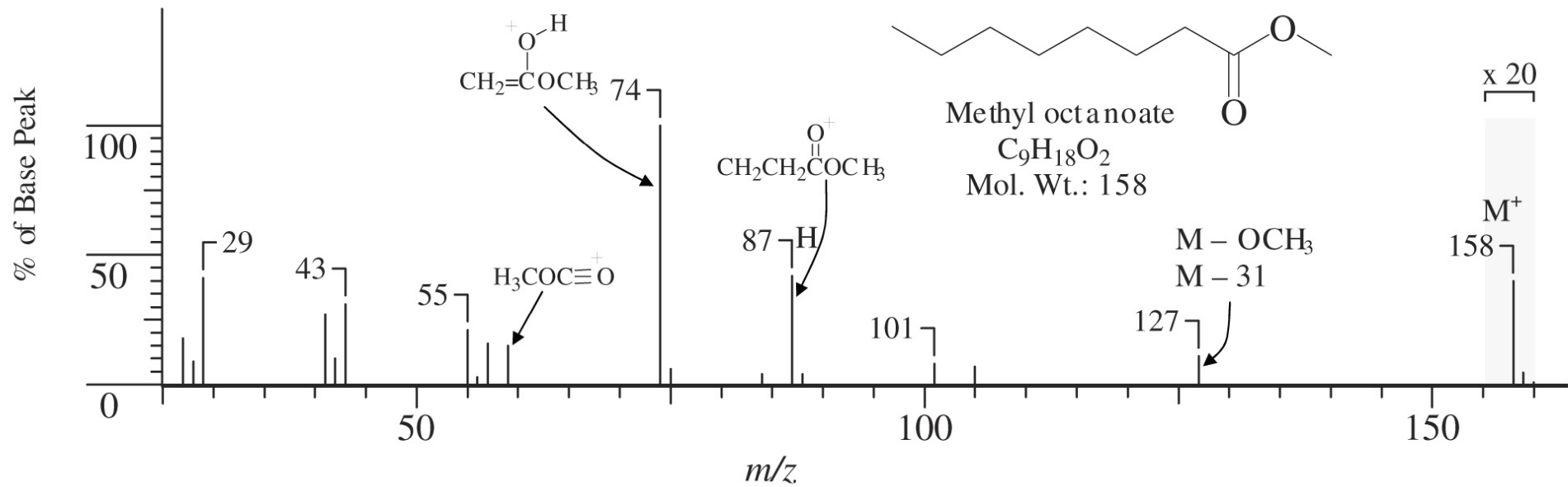
Ácido Decanoico



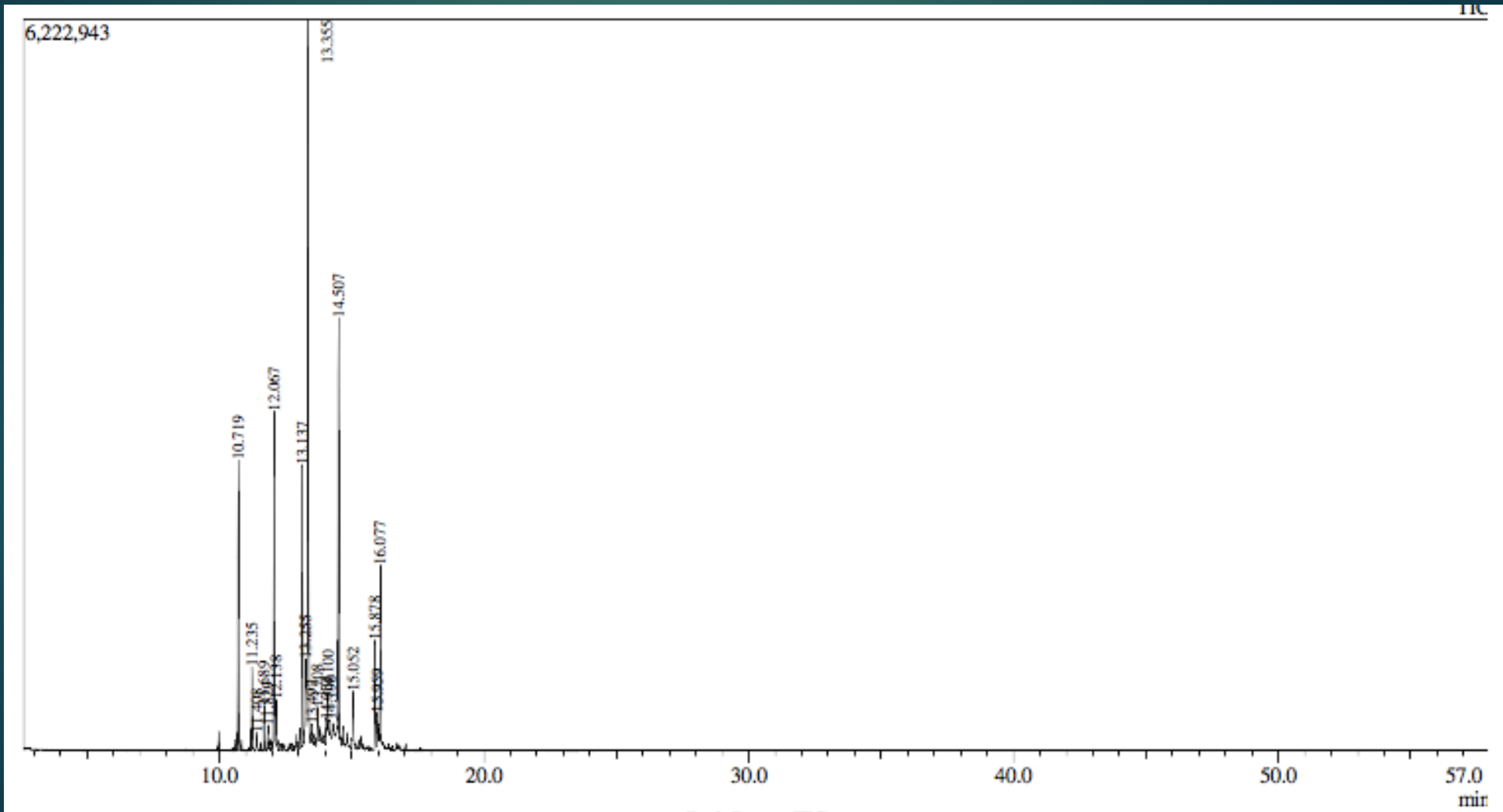
p-Chloroacetofenona



Octanoato de metila



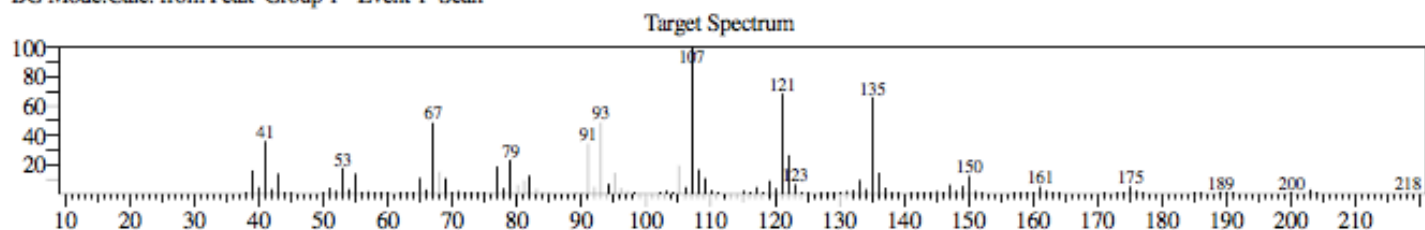
Vida real



Peak Report TIC							
Peak#	R.Time	L.Time	F.Time	Area	Area%	Height	A/H Name
1	10.719	10.675	10.767	4238813	8.65	2451011	1.73 Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-m
2	11.235	11.200	11.275	1238631	2.53	716601	1.73 .gamma.-Elemene
3	11.408	11.275	11.658	564485	1.15	155606	3.63 Aromandendrene
4	11.689	11.658	11.725	653915	1.33	386397	1.69 (1R,9R,E)-4,11,11-Trimethyl-8-methylenebicy
5	11.829	11.783	11.867	410593	0.84	203856	2.01 Guaia-1(10),11-diene
6	12.067	12.017	12.108	5129887	10.46	2861114	1.79 Benzofuran, 6-ethenyl-4,5,6,7-tetrahydro-3,6-
7	12.138	12.108	12.175	761753	1.55	399320	1.91 .alpha.-Guaiene
8	13.137	13.100	13.183	4547327	9.28	2394624	1.90 (-)-Spathulenol
9	13.255	13.225	13.308	2609732	5.32	741639	3.52 Globulol
10	13.355	13.308	13.433	13226833	26.98	6173377	2.14 3,7-Cyclodecadien-1-one, 3,7-dimethyl-10-(1-
11	13.492	13.433	13.675	524678	1.07	171142	3.07 Cryptomeridiol
12	13.708	13.675	13.742	556074	1.13	292812	1.90 Isoaromadendrene epoxide
13	14.033	14.000	14.075	564681	1.15	195539	2.89 .alpha.-Cadinol
14	14.100	14.075	14.142	831533	1.70	398089	2.09 Globulol
15	14.190	14.142	14.225	341505	0.70	159874	2.14 1H-Cycloprop[e]azulen-7-ol, decahydro-1,1,7-
16	14.507	14.458	14.542	6367740	12.99	3480977	1.83 3,7-Cyclodecadien-1-one, 3,7-dimethyl-10-(1-
17	15.052	15.025	15.100	747358	1.52	430805	1.73 trans-Valerenyl acetate
18	15.878	15.833	15.925	1739086	3.55	921672	1.89 3,7-Cyclodecadien-1-one, 3,7-dimethyl-10-(1-
19	15.959	15.925	16.033	1044436	2.13	292448	3.57 Curcumenone
20	16.077	16.033	16.133	2927101	5.97	1526444	1.92 Fragranyl isobutyrate
				49026161	100.00	24353347	

<< Target >>

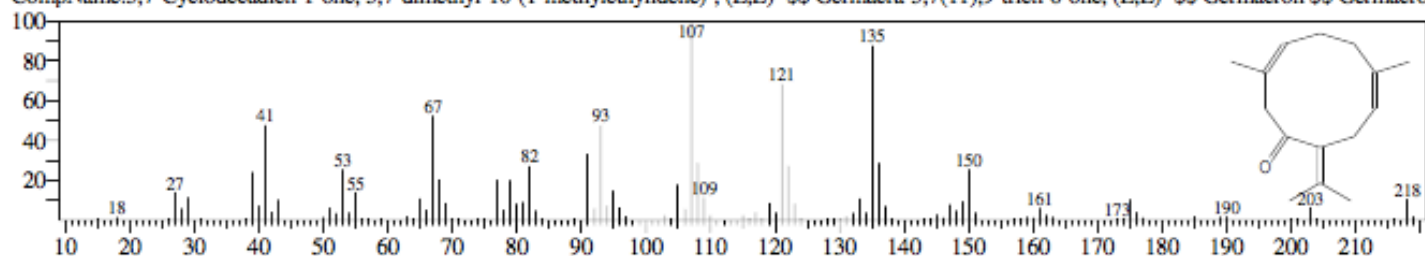
Line#:10 R.Time:13.358(Scan#:1292) MassPeaks:127
RawMode:Averaged 13.350-13.367(1291-1293) BasePeak:107.05(621453)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



Hit#:1 Entry:21104 Library:NIST14s.lib

SI:93 Formula:C₁₅H₂₂O CAS:6902-91-6 MolWeight:218 RetIndex:1774

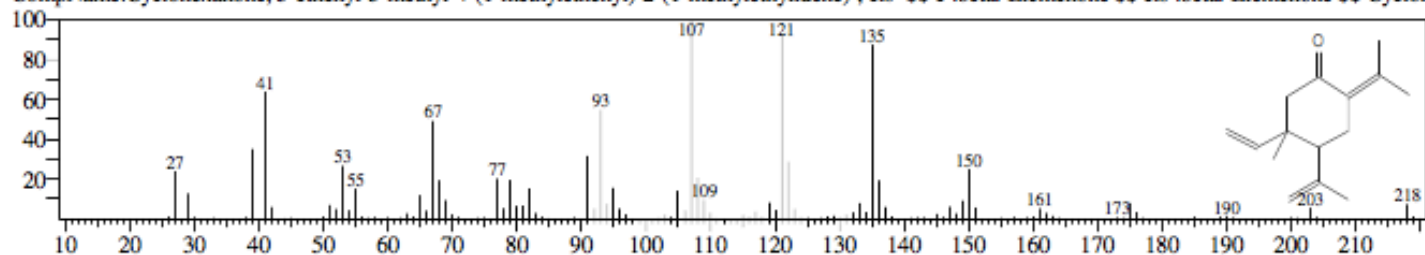
CompName:3,7-Cyclodecadien-1-one, 3,7-dimethyl-10-(1-methylethylidene)-, (E,E)- \$\$ Germacra-3,7(11),9-trien-6-one, (E,E)- \$\$ Germacron \$\$ Germacro



Hit#:2 Entry:60826 Library:NIST14s.lib

SI:92 Formula:C₁₅H₂₂O CAS:32663-57-3 MolWeight:218 RetIndex:1602

CompName:Cyclohexanone, 5-ethenyl-5-methyl-4-(1-methylethenyl)-2-(1-methylethylidene)-, cis- \$\$ c-beta-Elementone \$\$ cis-beta-Elementone \$\$ Cyclot



Hit#:3 Entry:21103 Library:NIST14s.lib

SI:92 Formula:C₁₅H₂₂O CAS:20303-60-0 MolWeight:218 RetIndex:1602

CompName:.beta-Elementone \$\$ (4S)-trans-.beta-Elementone \$\$ Cyclohexanone, 5-ethenyl-5-methyl-4-(1-methylethenyl)-2-(1-methylethylidene)-, (4S,5S)

